THE BOOK WAS DRENCHED

CRYSTALLISATION OF METALS

CRYSTALLISATION
OF METALS

BY
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BEING A COURSE OF ADVANCED LECTURES IN
METALLURGY DELIVERED AT THE ROYAL
SCHOOL OF MINES — IMPERIAL COLLEGE
UNDER THE AUSPICES OF THE
UNIVERSITY OF LONDON
IN FEBRUARY AND MARCH 1922

WITH A PREFACE BY
PROFESSOR H. C. H. CARPENTER, F.R.S.

TO THE MEMORY OF

MY FATHER

PREFACE

COLONEL N. T. BELAIEW, C.B., has been known
for some years as a talented investigator of the
crystal forms of metals. He has made a special
study of the macrostructure of steels, of Wid-
manstätten figures, and the structure of
Damascene steels. A pupil of the distinguished
Russian professor, D. K. Tschernoff, to whose
influence he pays a tribute in the present
volume, he has derived great inspiration from
him and the Russian metallurgist Anossoff, as
well as the English petrologist and metallo-
graphist Sorby. Colonel Belaiew's early investi-
gations were carried out at the Michael Artillery
Academy, Petrograd. At the outbreak of the
war in 1914 he was appointed to the command
of a battery in the Russian Army, and fought in
numerous engagements. After severe concus-
sion, he was invalided out of the Army and sent
to England, where, for the remainder of the
war, he rendered valuable services in connection
with the supply of munitions to the Russian
Army. Since 1915 he has been resident in
England, and has recently been able to resume

his metallographical studies. Advantage was taken of his presence in this country by the University of London, at whose invitation he delivered, in the spring of 1922, a course of lectures which forms the basis of this volume. The choice was a very happy one, and the lectures were delivered to a greatly appreciative audience at the Royal School of Mines.

The subject chosen by Colonel Belaiew is one both of scientific and industrial importance. On the one hand, metals exhibit certain peculiarities of crystallisation, giving rise, e.g., to characteristic skeleton, dendritic, and arborescent forms, which have been the subject of much study during recent years. Moreover, the investigation of reactions between metallic crystals has probably contributed more to a knowledge of the reactions between substances in the solid condition than has any other branch of physical chemistry. Much light has been thrown on the nature of diffusion in the solid state and on solid solutions themselves. On the other hand, the properties of metals are the properties of metallic crystals, and the behaviour of every metallic article used in the arts and industries depends upon the particular size, arrangement, texture, and composition of the crystals of which it is composed. For the most part these crystals are very small, and require for their investigation a special microscopic

technique. This is an important part of the new science known as " metallography." Colonel Belaiew, however, has very wisely insisted on the fundamental importance of a knowledge of the macrostructure of metals and alloys, and his lectures illustrate in a particularly striking way the intimate relation between the macrostructure and microstructure of any given alloy as regards its properties.

The present volume gives, for the first time, so far as the writer is aware, the presentation in English of the phenomena of the crystallisation of metals in a compact form by a Russian investigator. It has been his privilege during the past seven years to become somewhat intimately acquainted with Colonel Belaiew himself, and to enjoy frequent discussions on matters related to those dealt with in the lectures. He deeply appreciates the honour of having been asked to write the preface to Colonel Belaiew's book, and he would add his hope that it will be widely studied by natural philosophers, not only in this country, but wherever English is read and understood.

H. C. H. Carpenter.

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FOREWORD

THE Author would like to say how keenly he appreciates the fact that thanks to the kindness of the Senate of the London University he was given the privilege of lecturing on the *Crystallisation of Metals* at the *Royal School of Mines*.

The processes of solidification and crystallisation are intimately associated with the various areas and curves of the Equilibrium Diagram, and the Author would like to make special reference to the work of Sir William Roberts Austen, to whom we are indebted for our early knowledge of the Equilibrium Diagrams of Iron and Steel, as well as of many other alloys, and to Professor H. C. H. Carpenter, whose work (in conjunction with B. F. E. Keeling) on the Range of Solidification and the Critical Ranges of Iron Carbon Alloys, completed the " stability " of the Iron Carbon Diagram.

The Author's researches on crystallisation of steel were animated by the idea of bringing into closer harmony the processes of crystallisation with various areas of the Diagram. Studying the works of Sorby, who gradually was brought

from the study of the *macrostructure* of meteorites to the *microstructure* of steel, and learning how Anossoff likewise started from the *macrostructure* of Damascene blades, the Author felt deeply impressed by the importance of *macrostructure* and directed his early efforts towards obtaining large structures easily discernible with a naked eye.

These researches were started in 1906 at the Michael Artillery Academy, Petrograd, under the guidance of Professor D. K. Tschernoff, and the Author would like to state with the greatest reverence his indebtedness to his teacher and to his Alma Mater.

The results of these early researches were published in the Author's thesis *On Crystallisation* in 1909, and several photograms, reproduced on Plates I, II, III, IV, V, VI, VII, VIII, IX, XI, XVII, and XXI, are taken from that thesis.

For various reasons the Author was unable to resume his research work until early last year, when a small laboratory, and especially the invaluable assistance of his colleague Captain B. Brandt, enabled him to restart his researches on Pearlite. He would like to take this opportunity to express his gratitude to Captain Brandt for his untiring assistance in taking photographs and preparing slides. Photograms Nos. 18, 19, 20, 21, 22, 23, 24, 25, 28, 29, 30, 31, 32 (Plates XII, XIII, XIV, XV, XVI, XVIII,

XIX, and XX) were taken by Captain Brandt in the Author's laboratory, some of them in collaboration with the Author.

The Author would like to express his indebtedness to the Council of the *Iron and Steel Institute* for permission to reproduce from the Author's paper on Pearlite the photograms Nos. 18, 19, 20, 21, 22, 23, 24, and 25, on Plates XII, XIII, XIV, XV, and XVI ; to the Council of the *Institution of Aeronautical Engineers* for the photograms Nos. 3, 7, 8, 16, and 17 (Plates III, V, XI, and Figs. 26 and 30 in the text); to the Council of the *Institute of Metals* for the photogram Nos. 10 (Plate VII), 14 and 15 (Plate X) ; to the Council of the *Russian Economic Association* for Phot. 1 (Plate I) ; to the Keepers of the Wallace Collection for Phot. 34 (Plate XXI) ; and to the Senate of the *University of London* for having placed at the Author's disposal funds towards the publication of these Lectures.

Lecture I

CRYSTALLISATION FROM THE MOLTEN STATE

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CRYSTALLISATION FROM THE MOLTEN STATE

I. INTRODUCTION

AT the outset of a study of crystallisation let us, following Osmond's lead, ask first : " What is a crystal ? " (1).

Perhaps one of the many definitions given by crystallographers might be used as an answer. There are many of such definitions—too many maybe—so let us, instead of trying to make the most judicious selection, again follow Osmond's advice, and note that in any solid body there are two main elements to be taken into account : the *internal substance*, and the *external form*.

Let us assume that the molecules of a certain mass are arranged in regular formation ; such mass will be called " crystalline." The properties of such crystalline matter would vary around each point, but the variation will follow the same law in every point.

The fracture of such mass, instead of being irregular, like glass would present a smooth face

and so bring into evidence the existence of " cleavage planes."

Such smooth plane faces " with Nature's polish " (Haüy) would naturally attract our attention and direct it to the regularity of the external shape of a body built up of crystalline matter. But, however striking, the external regularity is only the result of the internal symmetry.

So the most important element is the internal symmetrical arrangement of molecules in space, which is now usually called the " space lattice." But the importance of the other element, the geometrical regularity of form, must not be minimised either, as it may be considered as one of the most striking manifestations of the internal symmetry. A body built up of crystalline matter, and possessing the form of a regular polyhedron, will be considered as a perfect or idiomorphic crystal. Any other volume of crystalline matter may be equally well described as a crystal, but to show the difference from the perfect crystal will be called an allotriomorphic crystal.

II. SPACE LATTICE

Let us imagine four points in space, A, B, C, and O. Let us consider the point O as the origin of co-ordinates and so place the co-ordinate

axes as to comprise the points A, B, and C
(Fig. 1).

Let the lengths of the axes be

$$OA = a, \ OB = b, \ \text{and} \ OC = c.$$

Let the interaxial angles be

$$BOC = a, \ COA = \beta, \ \text{and} \ AOB = \gamma.$$

In the most general case the distances a, b, c
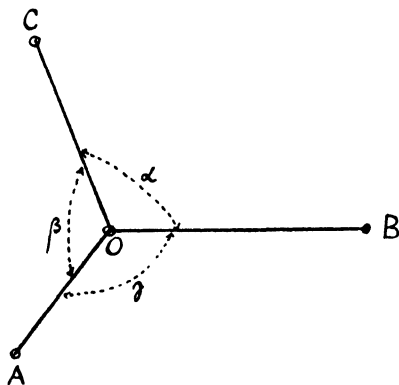
Fig. 1.—CO-ORDINATE AXES

are unequal, and the angles a, β, and γ are also
unequal.

Let us further suppose that every one of the
three other points is considered as the origin
of a similar system of co-ordinates, characterised
by distances a, b, c, and angles a, β, and γ, and
so on :

So long as a, b, c, and a, β, γ, remain constant

and the same, *the environment about any particular point is the same as about any other point.*

In spite of the inequality of the distances a, b, c, and of the angles α, β, γ, there is a certain regularity in the arrangement of points, the arrangement being similar around every point as a centre. If molecules were arranged in this way, such an arrangement would be considered therefore as a crystalline arrangement.

The assemblage of points or " space lattice " as just described is of the most general character and subjected to the minimum number of conditions. The symmetry of such a system is the lowest possible, and substances crystallising in that system belong to the lowest class, and are called *triclinic.*

Every additional condition, for instance, the equality of two or three angles, or axes, will increase the symmetry of the system, adding axes or planes of symmetry.

If all the three angles are right angles ($\alpha = \beta = \gamma = 90°$) and all the three distances are also equal ($a = b = c$), then the maximum possible symmetry is reached. Such system is called the regular or cubic, as the cube is the fundamental form of such system.

There are in all seven crystal systems of increasing symmetry between the triclinic and the regular, namely :

1. The *Triclinic* system, characterised by three unequally inclined unequal axes.

2. The *Monoclinic*, when any two of the angles are right angles.

3. The *Orthorhombic*, when all three angles are right angles, but the distance *a, b, c* remains unequal.

4. The *Tetragonal*, when all the three angles are right angles, and in addition two of the axial lengths are equal.

5. The *Trigonal*, with three equal and equally inclined axes (but not at right angles).

6. The *Hexagonal*, similar to tetragonal, but characterised by three equal axes lying in the same plane and inclined at 60° to each other and a fourth vertical axis.

7. The *Cubic* system, with three equal axes inclined at right angles. (2)

As metals mostly crystallise in the regular system, we shall consider that system only.

III. THE REGULAR OR CUBIC SYSTEM

The regular system is characterised by three equal axes inclined at right angles (Fig. 2).

The axial lengths or parameters are equal : $a = b = c$.

The interaxial angles are also equal : $\alpha = \beta = \gamma = 90°$.

The three axial planes, AOB, BOC, and COA, are planes of symmetry, i.e. planes dividing the crystal into two symmetrical parts, bearing one to another the same relation as the object to its mirror image. These three rectangular planes are called principal planes of symmetry.

By bisecting the angles a, β, γ, and their
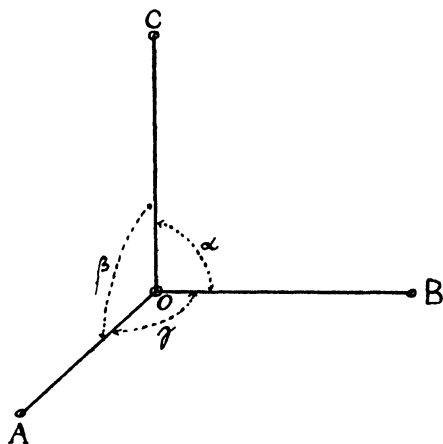
Fig. 2.—REGULAR CO-ORDINATE AXES.

supplementary angles by normal planes, six diagonal or secondary planes of symmetry are obtained.

Let us imagine a geometrical solid; for instance, an octahedron built up on the three axes a, b, c.

Let that solid be rotated about the axis a. As it is rotated through 360°, every time that the axis "a" coincides with another axis the

aspect of the crystal will be the same. As
shown on Fig. 3, it will happen four times.
Therefore the crystallographic axis " *a* " will
be a tetragonal axis of symmetry (Fig. 3).

Similarly, the axes *b* and *c* are also tetragonal
axes, and *the whole number of tetragonal axes,*
or axes of fourfold symmetry, *will be three.*
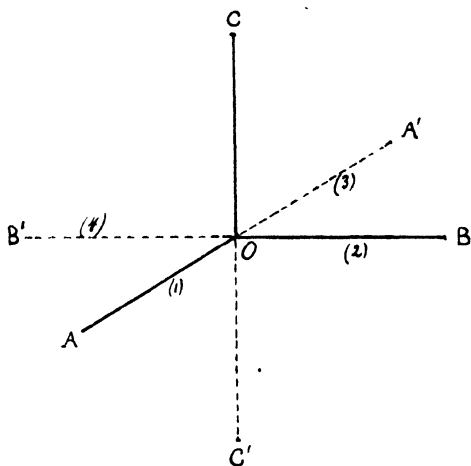
FIG. 3.—TETRAGONAL AXES.

There are besides *four trigonal axes of symmetry,*
and *six digonal axes,* these latter bisecting the
interaxial angles α, β, γ.

The large number of planes of symmetry, and
axes of symmetry (or rotations), shows how
perfect the molecular arrangement is in the
cubic system, which is therefore called the
regular system.

IV. The Cube and the Octahedron

Let us consider some of the main geometrical solids which could be built up on the three rectangular axes of the regular system.

The *fundamental,* or the axial plane form, is the cube (Fig. 4) or the regular hexahedron.

As a geometrical solid is said to be *regular* when its faces are equal regular figures, it follows that the six faces of the cube are all equal.   As
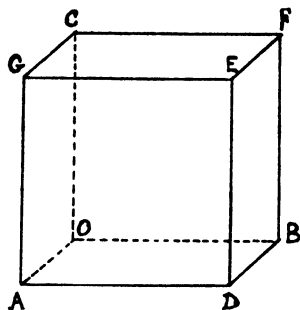
Fig. 4.—CUBE.

the axial angles are right angles, these figures are all squares.

The six squares are arranged in three pairs. Every pair of faces cuts one of the crystallo-graphic axes only, and is parallel to the other two.   The face ADEG cuts the axis *a,* and is parallel to the other two.   The intercepts of this plane are therefore *a,* ∞ and ∞ , or, assuming *a* = 1, 1, ∞ , and ∞ .

In crystallography, in describing a plane the

reciprocals of intercepts are used and are called *indices*.

So, for the plane in question, the indices would be 1, 0, 0. The other two planes would be (001) and (010). In the three faces lying behind the index one is considered to be negative.

The symbol of the front face (100) is taken as the symbol of the cube.
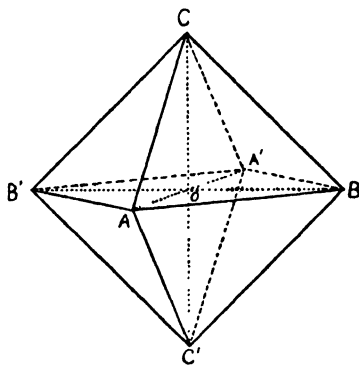
Fig. 5.—REGULAR OCTAHEDRON.

This system of indices was first introduced by W. H. Miller in his classical *Treatise on Crystallography* (3), and is now generally used.

The next important form is the parameter-form (111) or the regular octahedron (Fig. 5).

An octahedron is a geometrical solid bounded by eight faces. Each of the eight faces is an equilateral triangle. There are six similar solid angles and twelve edges of equal length. Two

edges belonging to the same face meet each other at an angle of 60°, two edges belonging to different faces form an angle of 90°.

The angle between two adjacent faces is 70° 31′ 44″, and is called the octahedral angle. The angle between two intersecting opposite faces is the supplement of the octahedral angle and is therefore 109° 28′ 16″.

Any two opposite faces are parallel, and the eight faces of the octahedron may be grouped into four pairs.

Metals crystallising in the regular system usually assume the form of either the cube, or that of the octahedron, or of their combination.[1]

Moreover, during the growth of the crystals, instead of regular forms the imperfect are more readily developed. In their shape these follow either the *axes,* or the *faces* of their respective forms. In such skeleton forms the angles still are the angles of corresponding geometrical solids.

Therefore, it is well to always bear in mind the few stereometrical relations already indicated. They will meet us at every turn.

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[1] The remaining forms are the *rhombic dodecahedron* (110) with twelve faces parallel to the diagonal planes of symmetry, the *hexaxis octahedron* (321) with 48 faces, the *icosatetrahedron* (211) with 24 faces, the *triaxis octahedron* (221) and the *tetraxis hexahedron* (210).

V. The Vectorial Crystallisation Force and Surface Tension

The force which causes the molecules of a substance to arrange themselves in regular pattern may be called crystallising or crystallisation force ; it is in the first instance a directive force, and is therefore usually spoken of as the *vectorial crystallisation force.*

To show how great that force can be, the bursting of rocks by the growth of ice-crystals may be cited.

Let us imagine a cooling liquid. When the freezing point is reached the liquid enters the area of such temperatures when the rearrangement of molecules in a rigid structure must begin. The impulse towards such rearrangement will be the greater the greater the undercooling of the liquid. A certain degree of undercooling is necessary to start the process, but the degree of initial undercooling will manifest itself in the amount of " released " crystallisation force. This in turn will cause the process of crystallisation to proceed with a greater or smaller *linear velocity*.

The numerical values of the velocity of crystallisation at temperatures close to the freezing point are considerable, especially in metals.

The point where the rearrangement of mole-

3

cules or " crystallisation " starts may be called the centre or the " nucleus " of crystallisation. The number of such nuclei depends on the properties of the crystallising matter, and on the conditions of cooling. According to Tamman's experiments, the velocity of appearance of the nuclei per unit of volume reaches a maximum at a certain temperature (below the freezing point) which is characteristic for every substance (4).

When the crystallising substance has entered an area where both the velocity of the appearance of the nuclei (spontaneous velocity of crystallisation) and the linear velocity are at their maximum value, then the most favourable conditions for a quick crystallisation will have been reached.

The process of rearrangement of molecules will then proceed at the greatest possible speed, almost instantaneously, and the orienting power of molecules will be taxed, so to say, to their utmost capacity.

If the process were to proceed in such a medium where no forces would oppose the rearrangement—a medium where any kind of friction or of viscosity would be excluded—then we could possibly expect that ultimately, in spite of the violence of the process, ideal fully developed crystals would appear.

But that is not the case. Every crystallisa-

tion proceeds in a medium where a certain internal pressure always exists. As a consequence of that pressure the growing crystal will be subjected to a surface pressure, called *surface tension.* The values for that tension are comparatively high, especially in metals.

Let us imagine a rapidly growing crystal. As the crystal grows, all the faces grow accordingly, and as they grow they are subjected to always increasing pressures, which will steadily hamper the free development of the faces of the crystal, and instead of fully developed regular crystals, other forms, distorted, or of quite unexpected appearance will occur.

So the process of crystallisation is controlled by the main influence of these two forces : the vectorial crystallisation force, and the force of surface tension.

VI. Regular Forms, Single Crystals, Tschernoff's Steel Crystal

Let us imagine a crystal growing slowly and undisturbed in a solution. Further, let us assume that the concentration of the mother liquor is the same on all sides of the crystal, and that the growth proceeds with the same velocity in all directions. Under such favourable conditions we may expect that all the faces will be equally developed and that a perfect idiomorphic crystal will be formed.

With salts the best procedure seems to be to place a small crystal on a thin silk thread in a beaker of not too supersaturated solution.   If every care is taken against draughts of air, rapid change of temperature, and the intrusion of dust, and so on, very regular and rather large crystals (for instance of alums) are sometimes obtained.

On the other hand, it is quite obvious that
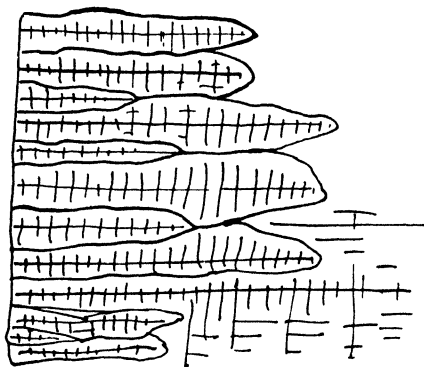
FIG. 6.—GROWING STEEL CRYSTALS.
(After Tschernoff.)

during the solidification of metals from a molten bath such, or like conditions, are impracticable, and idiomorphic crystals of metals are very rare.

However, it is possible to obtain crystals from the molten state even from metals with such high points of fusion as iron and steel.   These crystals are usually found in the cavity of large ingots in the portion which solidifies last (5).

PLATE I.
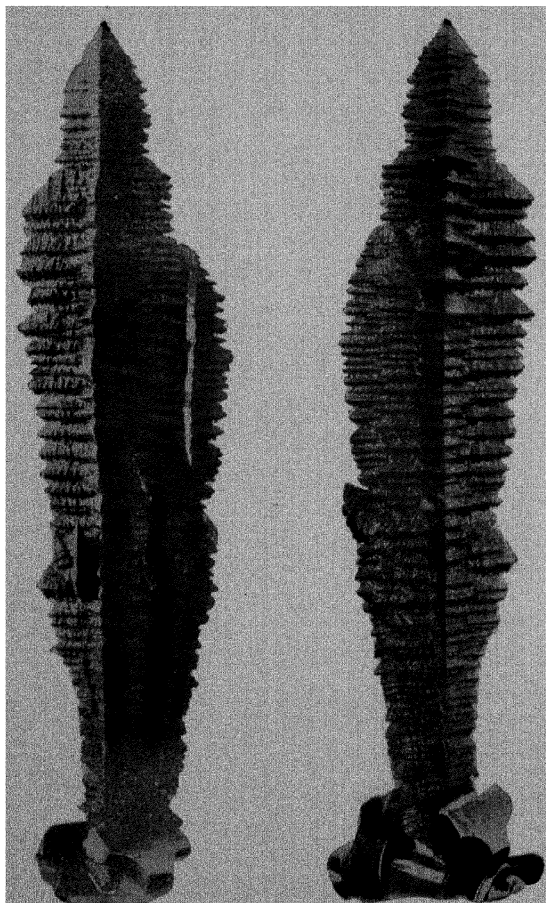
PHOT. 1—TSCHERNOFF'S CRYSTAL.
$C = 0.60\% - \times \frac{1}{3}$.

As they grow normally to the cooling surface one of the axes, parallel to this normal, is more developed than the others, and the crystals assume the shape of elongated aggregates of octahedrons so to say embedded one in another (Fig. 6).

The famous Tschernoff's crystal, more than 15 inches in size, was found in the upper portion of the pipe in the sinking head of an ingot of
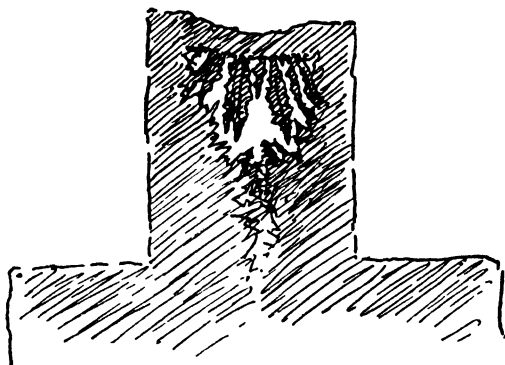
FIG. 7.—STEEL CRYSTALS IN THE SINKING HEAD OF 100-t. INGOT.
(After Tschernoff.)

soft open-hearth steel weighing about one hundred tons (Plate I, Phot. 1).

As the level of the liquid steel had been gradually lowered through the contraction of the solidifying metal below, new successive layers were deposited on the growing crystal, step by step (Fig. 7).

It is interesting to notice that in that case crystallisation seemed to proceed not con-

tinuously, but by pulsations or leaps, and that perhaps that is a general occurrence.

The external shape of Tschernoff's crystal makes it quite clear that under favourable conditions metals like salts can deposit single crystals of large size, with well-developed faces. If this crystal is like a multitude of octahedra embedded one in another it is because the growth started not from the middle of the liquid but from the walls of the cavity. Still, all the octahedra in the main crystal have one common axis which shows their common origin.

Salts, alum for instance, under similar conditions would deposit crystals exactly like the Tschernoff crystal.

In both cases crystals would be built up on three rectangular axes and bounded, under favourable conditions, by plane faces meeting one another under the octahedral angle of about 70°.

It is not only important, but wonderful to observe that substances so widely different as alum and steel would crystallise in analogous conditions exactly like each other, and to such an extent that a photograph of one might be mistaken for the other.

And that complete analogy in the external shape is only the result of the main fact that both substances belong to the same crystalline

system, and molecules of both are arranged in similar space lattices.

VII. The Growth of the Crystals— Skeleton Forms

The perfect symmetry of an idiomorphic crystal—of a rock crystal, for instance—would make one suppose that every plane face grows by regular deposits of layers of molecules one after another.

The difficulty of obtaining regularly developed crystals tends to show that to ensure such regular deposition many conditions have to be complied with, all of them having the object of ensuring the equal concentration of the mother liquor around all the faces, and consequently a steady and even supply of the " building substance."

As shown in preceding chapters, crystals can grow but *slowly*, if, so to say, they are expected to develop their faces regularly.

What, then, would have happened if time were denied and the crystallisation proceeded rapidly ? Then, as is always the case when there is not enough of what many want, some would have received preferential treatment. In the case of a growing crystal some *directions* must be brought into evidence and " filled úp " before the others, just as in an iron concrete structure the iron skeleton is placed first.

In the crystal the directions of " first import-
ance " are marked out by the geometry of solids
as *axes*, and there must be a strong probability
that axes will be traced first.

Now, what are the facts ?

Let us quote Professor Tschernoff, who de-
voted himself so much to the study of crystallisa-
tion :   In his lectures on Metallography he
describes the crystallisation of salts in the
following words :

" When studying under the microscope with
high magnification the formation of salt crystals
as they separate from their solutions, we note
that the growth of crystals from certain nuclei
manifests itself in a rapid, nearly simultaneous
appearance of axes, branches, and even planes,
starting in definite directions in accordance with
the crystallographic axes of the growing crystals.
From the principal axes will branch off axes
of the first order ; from these, axes of the second
order, and so on.   This takes place in such rapid
succession that it is impossible to trace the
formation of every individual branch.   The
rapidly forming branches gradually thicken and
elongate, and as a result meet neighbouring
branches and grow together " (6).

A certain number of such branches will soon
form a beam-like structure, or a crystal skeleton,
where the crystallographic axes are translated
into actual beams, or rods, by Nature's hand.

Dr. Knop, who made many interesting observations on the growth of crystals, in one of his works printed in 1867 (7), describes the crystallisation of ammonium chloride from aqueous solutions at low temperatures. He graphically depicts how first the regular axial cross is formed
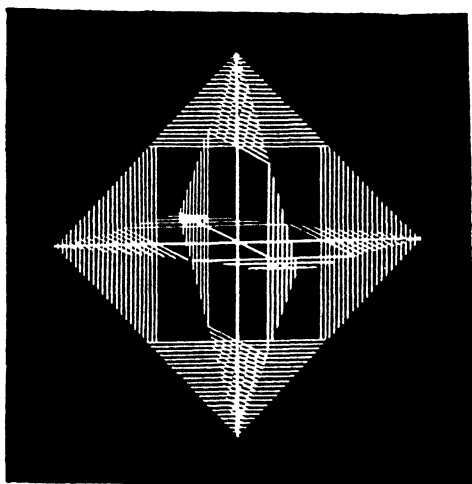
FIG. 8.—OCTAHEDRAL CRYSTALLISATION.
(After Knop)

and how the axes of the second and third order successively branch off (Fig. 8).

Nearly the same words are used by Morozevitch to describe the crystallisation of magnetite from supersaturated solutions.

He speaks of three main " rods " forming the octahedral cross, of the secondary and tertiary

axes, all of them tending first to form a skeleton-like " space lattice," and then, circumstances permitting, to fill it up and to complete the structure of the crystal (8).

These few examples could be multiplied and substantiated, but they make sufficiently clear, from actual observation, how the building up of a crystal goes on and what directions are the first to be filled up in that " Nature's architectural structure."

VIII. Skeleton Forms in Metals

Usually, if the formation of a crystal proceeds as just suggested, it would be most natural to expect to find such samples where the retreating mother liquor had left the " skeleton forms " naked and unattired.

More particularly could we expect to meet such skeletons rapidly crystallising substances, i.e. possessed of great *linear velocities of crystallisation*. As just mentioned, this is the case with metals. Even in the natural state copper, gold, and silver appear in such forms.

Copper, and more particularly iron, as being manufactured in large masses from early days, must have provided us with such structures, and indeed we owe the first description of such formation to a French ironmaster of the eighteenth century—Grignon (9).

Grignon's papers (he was also a correspondent

of the Paris Academy of Sciences) long remained unnoticed, and only Osmond made them known to metallurgists in his treatise *On the Crystallography of Iron* (10).

" Grey cast iron " says Grignon, " when in a perfect condition gives a very regular crystallisation, every crystal being distinct and isolated." He gives then a detailed description of the crystals in some very curious drawings (Figs. 9 and 10).
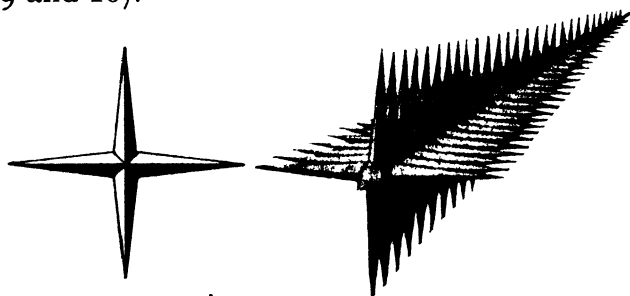
FIG. 9.—A CAST-IRON CRYSTAL.   FIG. 10.—SAME CRYSTAL VIEWED
    (After Grignon.)   OBLIQUELY.
(Osmond, *Sur la Cristallographie du Fer*, fig. 3.)

These figures show that Grignon's crystals are *skeleton forms built up on the rectangular axes of the regular* system.

Grignon found his crystals in cavities where, as mentioned before, the retreating liquid leaves these " uncompleted " forms.

A detailed description of analogous steel growths is to be found in Tschernoff's treatise *On the Structure of Cast Steel Ingots* (1879).

He says: "When examining individual crystals under the microscope, we observe that they belong to the crystal skeleton class, with a maximum development of shoots parallel to the octahedral axes, one of them always being longer than the other two in the direction of the main growth, so that every crystal is a skeleton of a drawn-out square octahedron.

"Besides the shoots in the direction of octa-
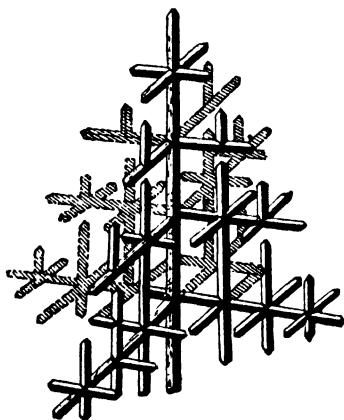
FIG. 11.—A SKELETON STEEL CRYSTAL.
(Tschernoff, *On the Structure of Cast Steel Ingots*, fig. 8)

hedral axes, or of the first order, there are secondary and tertiary shoots, frequently forming regular reticular beams of an octahedral crystal" (Fig. 11).

IX. DENDRITES—THEIR STRUCTURE

Let us suppose that a further stage in the crystallisation is reached, and the "beams and

rods " are beginning to be covered with further layers of crystallising matter. The whole, then, will begin to look more or less like a tree, and will be called a " *dendrite*."

Grignon, again, was the first to notice that the small crystals (in cavities) " . . . present under a magnifying glass the appearance of a small metallic forest, made up of trees with quaternary branches."

Dendrites may be considered as an intermediary form between crystal skeletons and fully developed crystals. It must be observed, however, that both skeletons and idiomorphic crystals occur very seldom, and therefore, when we come across metallic crystals, we usually find dendrites.

There is another reason why the study of dendrites is important—it is because the solidification of metals from the molten state, as first shown by Tschernoff, proceeds by the formation of crystal skeletons, and that subsequently an ingot is made up of juxtaposed and interlocked dendrites.

To prove that statement, extensive experiments were undertaken by the lecturer in the course of the years 1907–08. His working hypothesis being that slowness of cooling is one of the principal factors in the production of well-developed crystals, every care was taken to allow the alloys prepared to cool down slowly and undisturbed (11).

For this purpose the crucible method was
adopted, and after melting, the alloys were
allowed to cool down in the crucible together
with the furnace.

About twenty alloys of carbon steel with a
carbon content varying between 0·40% and
2·3% were prepared.

For the purpose of investigating the crystalli-
sation from the molten state or *primary crystal-
lisation*, external crusts were cut off from each
alloy.

There, preserved from oxidation by the layer
of slag, the most perfect picture of dendritic
crystallisation unfolded itself.   Long crystalline
axes of the first order stretched across the entire
alloy from one periphery to the centre ; these
branched off into secondary axes, perpendicular
to them, and then into tertiary axes, forming
tetragonal stars, just like Grignon's crystals.
A conglomeration of such stars formed the
long axes on the surface of the alloy (Plate II,
Phot. 2).

It must be mentioned that as there was
nothing to hinder the growth of the crystals
in the direction of external surface, all the
" axes " were standing out in relief.

At larger magnifications it may be easily seen
that these axes intersect themselves exactly at
right angles (Plate III, Phots. 3 and 4).

The same picture of primary crystallisation

PLATE II
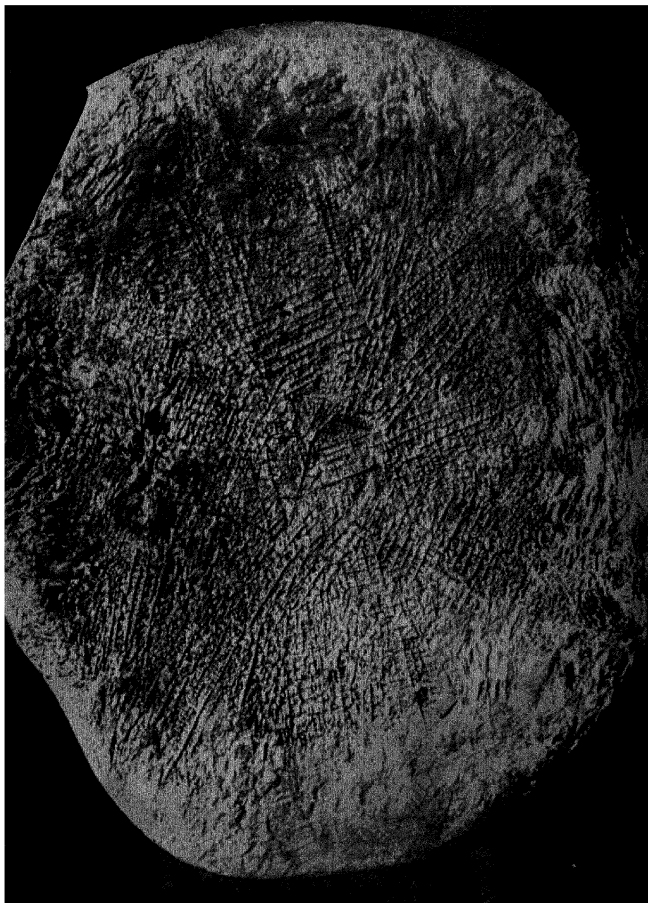
PHOT. 2.—" PRIMARY CRYSTALLISATION."
Alloy No. 2—C = 2·27%— × ¾.

PLATE III.—" PRIMARY CRYSTALLISATION."
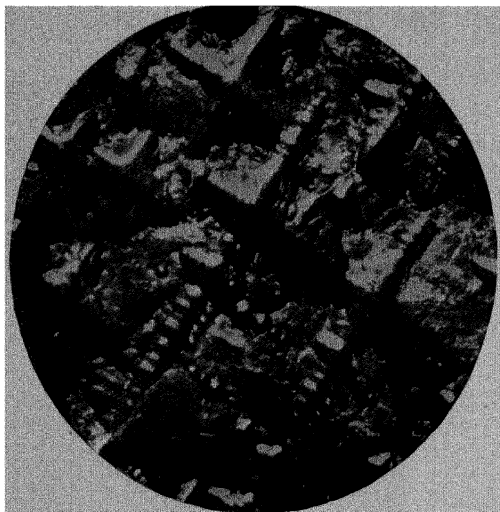
PHOT. 3.—STEEL DENDRITES ON THE DAY SURFACE OF THE ALLOY NO. 2
× 10.
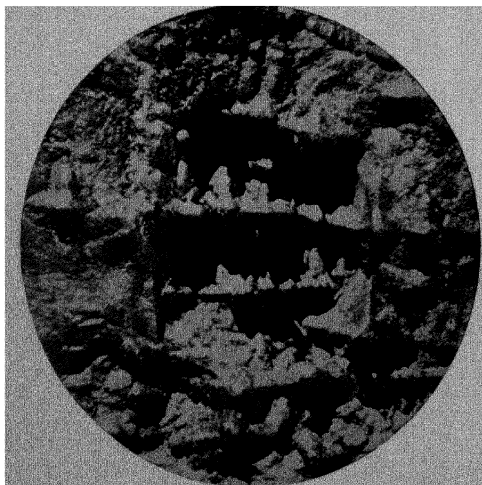
PHOT 4.—TWO DENDRITES BRIDGING A CAVITY.
× 10.

may be brought out by suitable etching on polished surfaces. Using a special reagent Mr. N. I. Belaiew, at the Poutilov Works, succeeded in a remarkable degree in bringing out the inner structure of dendrites, the " Dendritic Structure " (12). Reproduced below
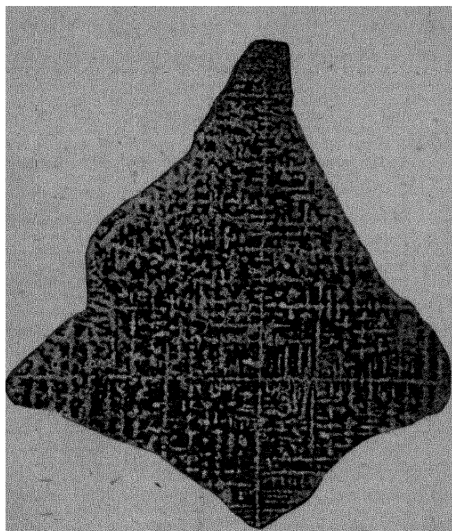
FIG 12.—CROSS SECTION OF A STEEL CRYSTAL × 2.
(Portevin et Bernard, *La Macrostructure de l'Acier*, fig. 3)

is a transverse section of a steel crystal after Portevin, etched by the " Stead-Le Chatelier " method (Fig. 12).

This macrostructure of the alloy is equally important both from the practical and from the theoretical point of view.

From the former it is important to bear in

mind that many properties of a finished article are to be traced down to the dendrites of primary crystallisation ; from the latter, let us say, the crystallographic one, that structure shows not only that every metal is built up of crystals, but also how these crystals are in turn built up ; how their axes are related one to another, and how constant remain the interaxial angles.

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4

Lecture II

CRYSTALLISATION IN THE SOLID STATE

CONTENTS

LECTURE II

CRYSTALLISATION IN THE SOLID STATE

I. INTRODUCTION

THE study of the Crystallisation of Metals from the molten state leads to the conclusion that that process is controlled by the main influence of two forces : the *vectorial crystallisation force,* and the *force of surface tension.*

Under the influence of the former the re-arrangement of molecules into regular patterns starts from several centres or nuclei ; the rate of the appearance of such nuclei per unit of time is called, after Tamman, the *spontaneous velocity of crystallisation,* and depends on the properties of the crystallisation substance and on the conditions of cooling.

From these centres the process advances at a certain pace with, as it is called, a certain *linear velocity of crystallisation.*

It has been further demonstrated that the actual rearrangement, or what might be called the " growth of the crystal," proceeds but seldom uniformly in all directions, and that usually

in the first instance crystalline axes are marked
out and crystal skeletons formed. Subse-
quently, new layers of crystallising matter
are deposited as so many " coats of paint "
and the crystal skeletons assume more and
more a tree-like appearance, becoming what is
known as " dendrites " (Fig. 13).

If, up to the end of solidification, the " den-
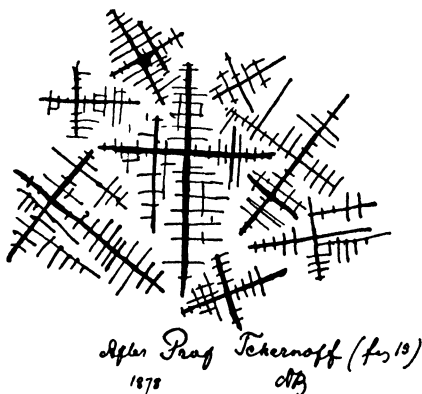
FIG. 13.—DENDRITIC CRYSTALLISATION IN STEEL.
(D. K. Tschernoff, *On the Structure of Cast Steel Ingots*, fig. 15.)

dritic " character of crystals remains very
marked, and new branches are being con-
tinually formed, then, finally, when different
dendrites come into contact their branches
become interlocked, and the whole mass of the
solidified alloy may be considered as a number
of juxtaposed or interlocked dendrites mutually
limiting each other. The boundaries between
such dendrites on a section will present a rather

curious shape, outlining more or less the different primary, secondary, and tertiary branches (Fig. 14).

Such is the case of the structure of most metals after solidification when the velocities of linear crystallisation were great. The solidification structures of large ingots of steel are a good illustration of such a type.

FIG. 14.—PRIMARY DENDRITIC GRAINS.
(D. K. Tschernoff, *On the Structure of Cast Steel Ingots*, fig. 16.)

But we may suppose that after dendrites appeared and the whole volume of the solidifying alloy was, so to say, " divided up " in areas " controlled " by every dendrite, the subsequent crystallisation proceeded not so much as a formation of new branches as an addition of new layers to the already existing ones.

Then the sharpness of the outlines would be more and more obliterated, and the external

shape of the growing dendrites would approach the form of an irregular polyhedron, or even a sphere.

Such mode of solidification is typical in cases when the velocities of crystallisation are not very great.

As in metals the interval of solidification, or *primary* crystallisation, is considerable, the velocities of crystallisation become smaller and smaller as the process continues ; therefore, the usual type of boundaries between adjacent dendrites will be of a more simple kind, their outlines being the result, in the first instance, of the number and distribution of nuclei of crystallisation.

II. The Crystalline Grain—Its Shape and Properties

Let us assume that the process of crystallisation is going on according to the second scheme, and that more or less uniform layers of crystallising matter are being deposited round the nuclei of crystallisation. Let us further suppose that the number of nuclei is N, and from these the process starts with a certain constant and uniform linear velocity V. We may imagine that in the first instance spheres will ensue from every nucleus. The next stage will be that of spheres beginning to meet and boundaries being produced. Finally, the whole volume will

be evenly distributed between the nuclei in so many polyhedral grains.

The inner structure of every grain will depend on the crystallographic properties of the crystallising matter. The orientation of that matter will be uniform throughout every grain and vary from one grain to another. Every grain can therefore be considered as a crystal. As the external shape of the grain results from the conditions under which the matter crystallises, and bears no relation to the internal symmetry, the metal grain belongs to the class of *allotriomorphic crystals*.

What are the conditions controlling the shape of a crystalline grain ?

Let us assume that the N nuclei are evenly distributed in space ; then let us take on a section six nuclei, A, B, C, D, E, and F, equidistant from a central nucleus O (Fig. 15).

The boundaries between the central grain and the six neighbouring grains, as shown by Benedicks (14), will be the loci of points equidistant from the respective nuclei, and will form a regular hexagon.

Let us take now the case of nuclei similarly related, but of unequal linear velocities. Let, for instance, V_A, the linear velocity from the nucleus A, be greater than the velocity from other centres :

$$V_A > V.$$

Then the hexagon related to the nucleus A will be larger than the others, and larger at their expense. For instance, the central grain will become irregular, and one of its edges will be larger than the other (Fig. 16).

Let us take now the more general case of
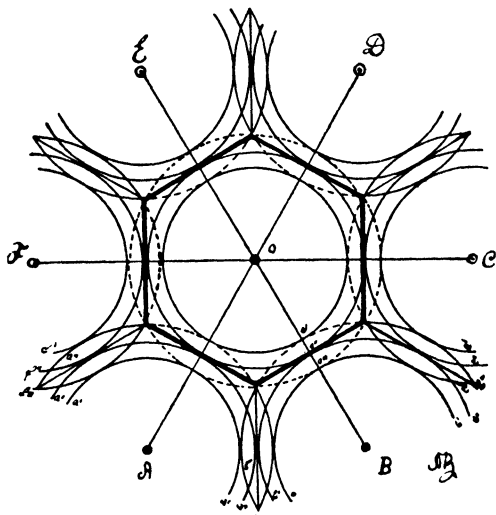
FIG. 15.—CRYSTALLISATION FROM EVENLY DISTRIBUTED CENTRES WITH EQUAL VELOCITIES.

nuclei being unequally distributed. The result would be that as indicated in Fig. 17—that is, an irregular hexagon (in the case of six nuclei distributed around the seventh).

In both cases a certain irregularity in the shape of the polygon is produced, but the boundaries remain the *loci of points equidistant from the nuclei*.
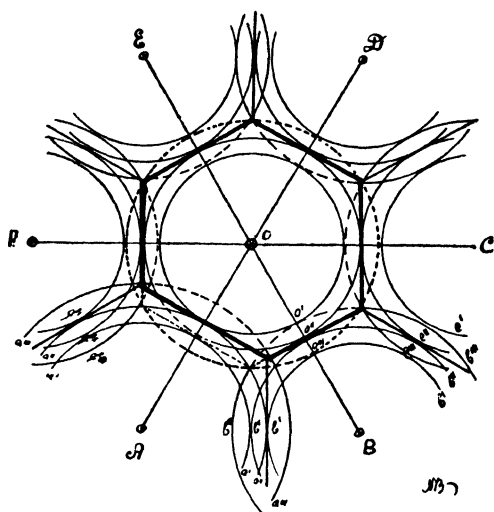
FIG. 16.—CRYSTALLISATION FROM CENTRES EVENLY DISTRIBUTED
WHEN VELOCITIES ARE NOT EQUAL.
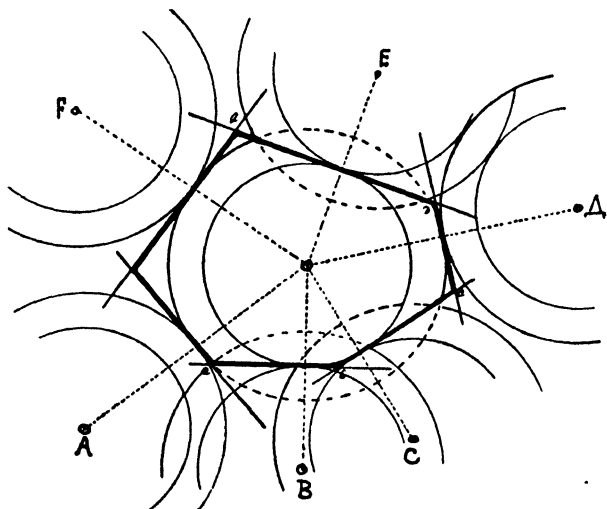
FIG. 17.—CRYSTALLISATION FROM CENTRES UNEVENLY DISTRIBUTED.

III. The Shape of the Grain, and the Homogeneous Partition of Space

The shape of the grain thus depends on the number and distribution of nuclei and on the linear velocity of crystallisation.

There are, however, two other factors influencing the shape of the grain : the condition of equal partitioning of space and the surface tension.

Following Professor Desch, we have always to bear in mind the important part which the surface tension plays during the crystal growth (15).

During the last stages of the formation of grains, just before the actual boundaries are formed, the rôle of surface tension would seem to be to favour the formation of such boundaries as would give a minimum superficial area for a given volume.

The problem of the homogeneous partitioning of space, quite naturally, was taken up by crystallographers. Fedorow published in the transactions of the Russian Mineralogical Society in the eighties several papers where his ideas on *parallelohedra*, or equal figures ranged parallel to each other, were expounded (16). The simplest of these figures is the *triparallelohedron,* which is the cube, the

last is the *heptaparallelohedron*, which is the cubo-octahedron.[1]

The same problem of partitioning of space, but in the most general form, was given a little later by Lord Kelvin in the " Proceedings of the Royal Society " in a memoir on the *Homogeneous Division of Space* (17). The cell which would have the minimum superficial area for a given volume was shown by him to be a parallel-faced cell of fourteen walls, eight of them hexagonal, and four quadrilateral. Lord Kelvin called such a cell a " tetrakaidecahedron."

It is interesting to observe that the most simple form of such a cell is also the cubo-octahedron, thus making Kelvin's tetrakaide-cahedron identical with Fedorow's hepta-parallelohedron.

It would seem, therefore, as if every grain in the last stages of its formation would be subjected to forces tending to modify its shape so as to make it comply with the structure of such a " normal " cell.

IV. The Polyhedral Structure in Metals and Alloys

If the outer form of the grain bears no relation to its internal symmetry, but is merely in the

---

[1] The cubo-octahedron is a combination of the cube and the octahedron, and may be obtained by truncating (symmetrically replacing) the corners of either the cube or octahedron.

nature of a " compromise " (18) between the opposing forces of crystallisation and surface tension, then it is to be expected that the outer shape of grains of different metals would be identical, if the conditions of cooling are identical.

As an illustration, the structure of pure metals, as gold (Fig. 18), copper (Fig. 19), and iron
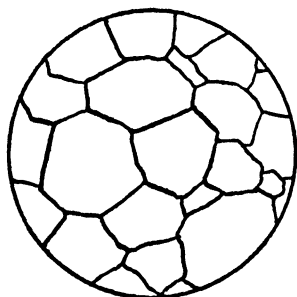
FIG. 18.—PURE GOLD. CAST (× 30).
(After Andrews.)
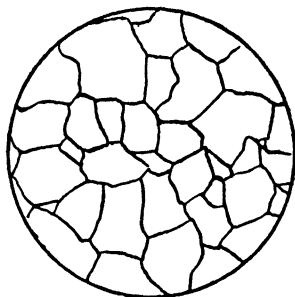
FIG. 19.—PURE COPPER (× 60).
(After Langenberg.)
(Sauveur, *Metallography*, fig. 106.)

(Plate IV, Phot. 5), might be given. In every case of a section more or less regular polyhedra would occur. So frequent is that structure that it is considered as a special class, and called sometimes *cellular* (after Osmond) or, more usually, *polyhedral*.

It must be noted that in describing the genesis of that structure no limitations were presupposed. Therefore, the same polyhedral structure would occur under similar conditions

PLATE IV.
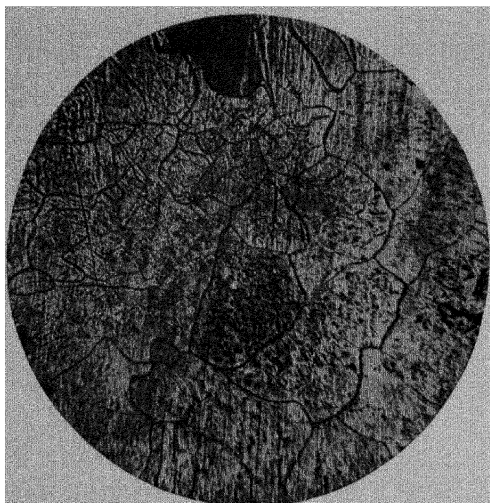
PHOT. 5.—PURE WROUGHT IRON FROM ARTIN.
Polyhedral Structure of Ferrite.— × 100.

PHOT. 6.—NETWORK STRUCTURE.
Alloy No. 5—Ferrite and Pearlite.— × 150.

whether crystallisation proceeds from the molten or in the solid state.

Let us suppose that the process of crystallisation is occurring two or more times in succession in the same body. For instance, a certain substance having crystallised from the molten state is undergoing one or more allotropic transformations, as is the case with iron.

As every allotropic transformation is starting from nuclei with a certain linear velocity it must be expected that such transformation would, under suitable conditions, bring out their polyhedral structure.

The meshes of the first polyhedral network may or may not be obliterated. In the second case, two or more networks might be seen.

On Phot. 5 of Plate IV two networks are shown as seen on a sample of pure wrought iron from Artin. As there is a difference in levels between the meshes of both, it is difficult to bring them out simultaneously on the same photograph. The second net, however, is seen sufficiently well on the upper part of the picture.

In iron alloys the same polyhedral structure can be brought into evidence either by special etching at high temperatures, where iron is in the so-called gamma state (Saniter, Osmond, Baykoff), or in certain alloy steels, as, for instance, nickel or manganese steels.

The gamma grain, in the author's opinion,

is further brought into evidence by the sub-
sequent deposits in the meshes of the network
structure, or by the so-called Widmanstätten
figures in the Widmanstätten structure.   In the
former case the outline, or the outer structure of
the grain, is made clear ; in the latter, the inner
structure, or the orientation and crystallo-
graphic habit of the crystalline matter.

V. Three Main Types of Secondary Structures

The inner structure of the crystalline grain
may be brought into evidence in several ways ;
there is the etching method, the X-rays method,
the polarisation of reflected light, and others.

There is, however, a method which besides its
simplicity has the advantage of showing simul-
taneously not only the orientation and the
habitus of the crystalline matter, but the
outlines of the grain as well. That is, *the
method of studying the structure of secondary
deposits.*

Many years ago Osmond wrote on this subject
as follows :

" When a liquid or solid deposits successively
several solid phases, the secondary and tertiary
deposits often preferably lodge between certain
of the crystallographic planes of the primary
deposit and thus illustrate its structure " (19).

So it is to be expected that under suitable conditions the inner crystallography of the grain may be made apparent ; for instance, the new deposits may lodge themselves parallel either to the *cleavage planes,* or to their *crystallographic axes.*

It would seem most natural, however, that in the first instance the boundaries of the grains would be marked out as a most convenient place to start the throwing out of the new crystals.

At the boundaries, where grains of different orientation meet, there must be a neutral zone— a kind of " no man's land "—where the crystalline matter cannot assume the orientation of either of the grains.

This thin layer of crystalline matter, which is considered by Rosenhain as in an " amorphous " state (20) would seem predestined to facilitate the appearance of the nuclei of the secondary depositions.

The recent papers of Professor Carpenter and Miss Elam (21) throw a good deal of light on the " boundary conditions " during recrystallisation, and we have to look to them for a further explanation of these most interesting phenomena.

However, the throwing out of secondary deposits or " secondary crystallisation " usually starts at the boundaries, and when it does not

there are always some special conditions, either in the process of cooling, or in the character of primary deposits, which force the crystallisation process to proceed in another way.

Let us consider the former case. First, a thin layer of a new deposit will be formed around every grain ; gradually that layer or film will become a kind of envelope. On a section, owing to such envelopes, the polygonal boundaries between the grains will look like so many " meshes " and the whole structure will assume a cellular or " network " character.

If the whole of the secondary deposit had time to segregate in this way, a pure " network " structure would ensue. The main condition, therefore, is a relation between the size of the grain and the speed of the secondary crystallisation as would make such a segregation not only possible, but the most likely.

It is easy to see that the larger the size of the grains, the more difficult it is to expect that the whole of the secondary deposit would collect at the boundaries.

If, for instance, the process were to proceed at a more accelerated pace, a certain proportion of the deposit would be forced to crystallise out " on the spot "—that is, not at the boundary, but in the middle of the grain. In such a case the habit and orientation of the crystalline matter would be the dominant factors, and

the deposits would arrange themselves parallel to the cleavage planes.

In another instance it might be supposed that another crystallographic element, the axes of the crystals, would play a similar rôle, lending, so to say, certain " advantages " to the deposits to remain where they were. Then a structure, reminding one of crystal skeletons, would appear.

So three main types of secondary structures might be anticipated ; first, the *network, or cellular, structure* marking the outlines of the grains ; then, two, so to say, " *crystallographic structures,*" exhibiting the inner symmetry of the crystalline substance of the grain :

> (*a*) with deposits lodged parallel to the cleavage planes, as the *Widmanstätten structure,*
>
> (*b*) when secondary deposits are arranged parallel to the crystallographic axes, as, for instance, in the Tschernoff crystal (*Structure of Large Crystals*).

VI. Secondary Structures in Iron and Steel

The Iron Carbon Alloys may be taken to illustrate the various types of secondary structures.

In the interval between 1,500° C. and 1,150° C.

the solidification from the molten state, or " primary crystallisation," occurs (Fig. 20).

Primary crystallisation results in the formation of crystal skeletons, subsequently converted into " dendrites," so that every alloy on leaving

°C ALLOYS OF IRON AND CARBON
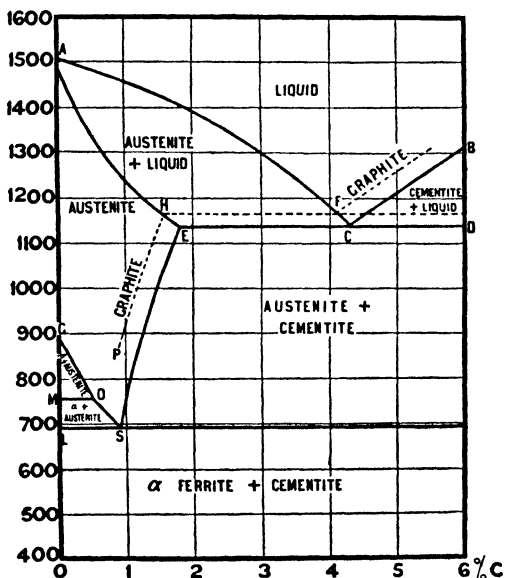
FIG. 20.—IRON CARBON EQUILIBRIUM DIAGRAM.

that area may be considered as being built up of dendrites, juxtaposed and interlocked with their branches. Every dendrite may be considered as a crystallographic unit.

The crystallographic unity of dendrites is destroyed in the austenitic or granulation zone

where new crystallographic units, the gamma grains, occur.

Between the temperatures of 900° and 690° the decomposition of the solid solution of carbon in iron (austenite) or *secondary crystallisation* occurs. In alloys with a carbon content higher than 0·85% the iron carbide Fe_3C (cementite) is gradually thrown out. In alloys with a lower carbon content pure iron (ferrite) is thrown out. In both cases the ultimate composition becomes 0·85% C, or that of the so-called " eutectoid " alloy (Howe). At a temperature of 690° C. eutectoid steel is being converted into alternate layers of the two components, cementite and ferrite (pearlite). Alloys containing more than 0·85% carbon are called, after Sauveur, " hyper-eutectoid," those with less than 0·85% " hypo-eutectoid." It may be added that such ferrite or cementite which separates before the eutectoid transformation is called the " pro-eutectoid " or " excess " or " free " element.

The separation of these elements will occur in a crystalline medium possessing a certain crystallographic habit and variously oriented in various grains.

As iron and steel crystallise from the molten state in octahedra, their structure will be brought into evidence by pro-eutectoid cementite and ferrite.

If the whole of such element is able to collect

around the boundaries of the grain, the " *network* " *structure* will occur, the meshes being formed of either cementite or pearlite, and the inner mass of the grain of pearlite (Plate IV, Phot. 6). Using a combined etching the author (22) succeeded in bringing out simultaneously the dendritic structure, resulting from the primary crystallisation and the meshes of the network of the secondary deposits (Plate V, Phot. 7).

If the interval of secondary crystallisation is covered too rapidly, a certain amount of the pro-eutectoid element will separate more or less instantaneously throughout every grain. Such separation will follow the crystallographic planes of the octahedron and result in *Widmanstätten structure* (Plate VII, Phot. 10).

In the absence of granulation, if, for instance, the secondary crystallisation were to follow the primary crystallisation, the pro-eutectoid elements would lodge themselves parallel to the axes of the crystals. In such a case, the pictures of the primary crystallisation and of the secondary would be quite identical. Such structure usually occurs either in semi-steels and white iron, or in isolated crystals. In an ordinary steel it is the result of slag enclosures (Plate V, Phot. 8).

In the alloys described by the author (23) the area of secondary crystallisation was passed very slowly; in some cases, for instance, the deposition of ferrite lasted not less than two

PLATE V.
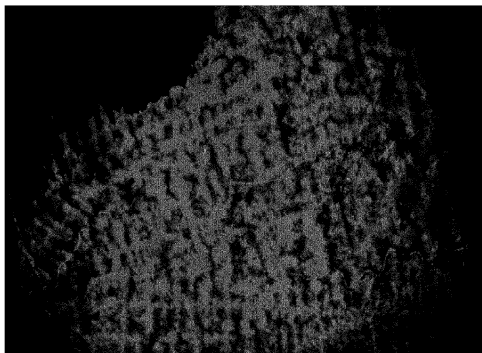
PHOT. 7.—THE DENDRITIC STRUCTURE (PRIMARY CRYSTALLISATION) AND
THE FERRITE MESH (SECONDARY CRYSTALLISATION)
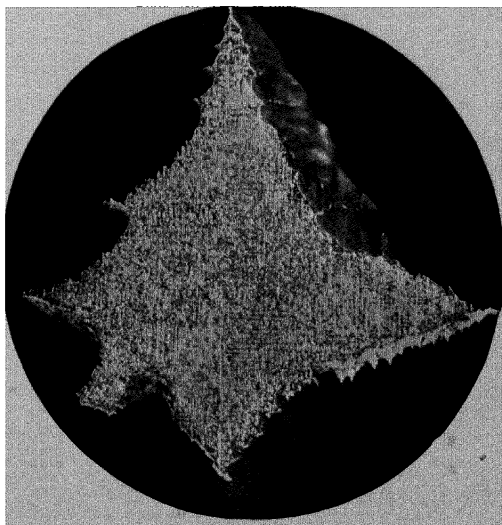
PHOT. 8.—" STRUCTURE OF LARGE CRYSTALS."
Tscheinoff's Crystal—C = 0·60%—Ferrite and Pearlite—× 1.

PLATE VI. SECONDARY STRUCTURES.
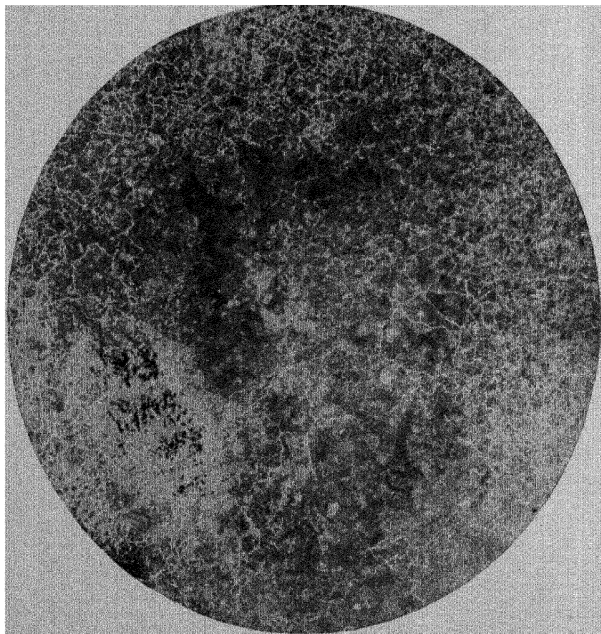
PHOT. 9 —" NETWORK STRUCTURE "
Alloy No 5—C = 0·60% —Ferrite and Pearlite— × ¾.

PLATE VII.—SECONDARY STRUCTURES.
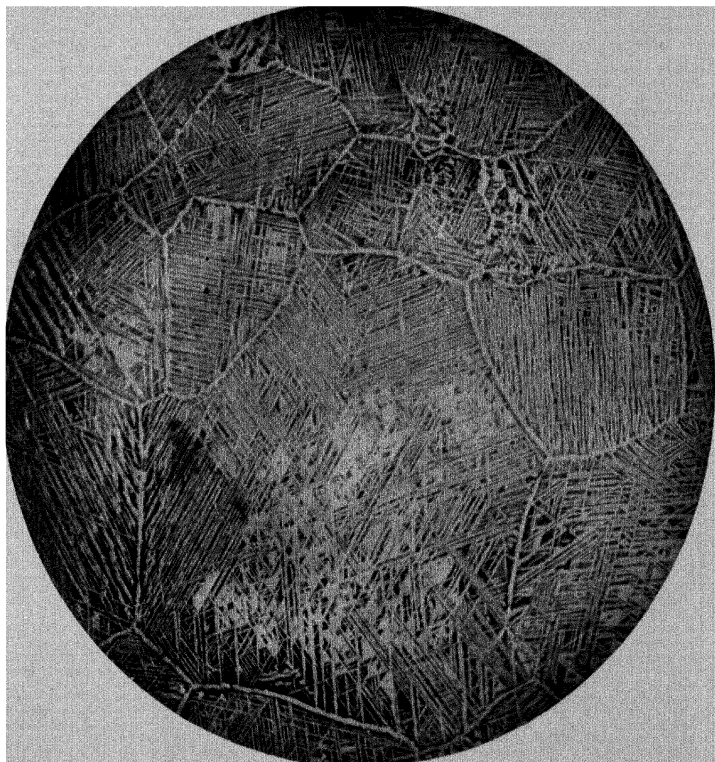
PHOT. 10 - "WIDMANSTATTEN STRUCTURE."
Alloy No. 8—C = 0·55%—Ferrite and Pearlite—× 5.

PLATE VIII.—SECONDARY STRUCTURES.
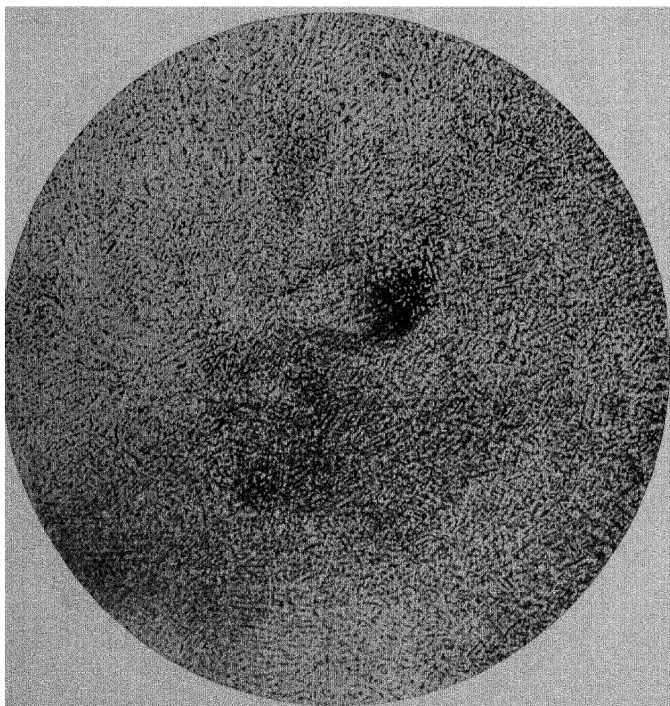
Phot. 11 —"STRUCTURE OF LARGE CRYSTALS."
Alloy No 1— $C = 1.80\%$, Pearlite and Cementite— × 1.

hours. As the process of granulation was also very marked, the granules being sometimes more than 7 sq. cm. in size, all the structures were very well developed and perfectly visible to the naked eye. The alloys Nos. 5 and 6 with 0·60% of carbon exhibit a " macroscopic " *network structure* ; the Alloy No. 8 (C = 0·55%) is a typical example of Widmanstätten structure (Plate VII, Phot. 10) ; whereas Alloys Nos. 1 and 2, more rich in carbon, show the " structure of large crystals " (Plate VIII, Phot. 11). The latter is also exhibited by the Tschernoff crystal. As the carbon content of this crystal, according to the author's analysis, is 0·60%, we have the three types of structures in cast steels *of the same carbon content* (Tschernoff's crystal, Alloys Nos. 5 and 8). This shows that the type of structure depends in the first instance not on the chemical composition, but on the conditions of cooling, and again *brings into evidence the importance of the crystallographic relation not only in crystals and isolated grains, but in ingots and, let us say, in every article manufactured of iron and steel or any other metal or alloy.*

VII. The Inner Structure of an Octahedral Grain

Metals usually crystallise in the systems with the highest degree of symmetry, i.e. in, the hexagonal and in the regular systems,

Such metals as iron, copper, gold, and silver crystallise in the regular system, and usually assume the form of either the cube, or of the octahedron. Iron and steel, for instance, when crystallising at high temperatures (in the gamma state) crystallise in octahedra ; this is the case with many brasses and other terrestrial alloys, and, moreover, of meteorites.

Therefore, the inner structure of an octahedral grain is of quite special interest.

As mentioned in Lecture I, an octahedron is a geometrical solid, bounded by eight faces. Each of the eight faces is an *equilateral triangle*. As in every crystal all faces are arranged in parallel pairs, we may consider that there are *four pairs* of faces.

We can also look at an octahedron as a four-sided pyramid. The base of that pyramid will be a square.

These figures, the triangle and the square, will appear on certain special sections. As for the general case of *any* section, let us consider first some simple geometrical relations.

Let us place the origin of Cartesian co-ordinates in the centre of the octahedron, and the three rectangular axes OX, OY, and OZ will coincide with the three octahedral axes (Fig. 21).

Let us now imagine four families of planes in space parallel to the four pairs of faces of an octahedron.

On the secant plane every family will produce a set of parallel lines, so that in all *four* sets of lines will be obtained. Let us call the angles between these four sets, A, B, C, and D. All four angles can be measured, but only three are independent, the fourth being their function ; for instance, $D = 180° — (A + B + C)$.

$$\angle ZOP_1 = \angle ZOP_2 = \epsilon = 54° 44' 8"$$
$$P_1 OP_2 = P_2 OP_3 = \delta = 70° 31' 40"$$
$$P_1 OP_3 = P_2 OP_4 = 2\epsilon = 109° 28' 16"$$
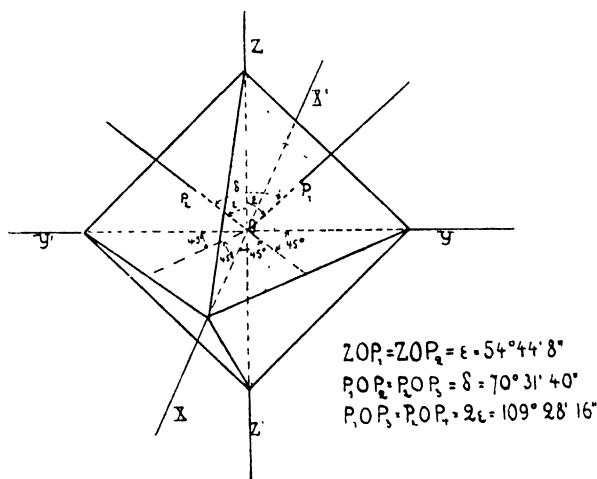
Fig. 21.—A REGULAR OCTAHEDRON.

If the same secant plane should meet another set of planes, similarly related to the faces of another octahedron, four other sets of lines would be produced and four other angles, A', B', C', and D', recorded.

Generally speaking, every family of planes parallel to the four faces of an octahedron will produce on a secant plane one and only one

combination of lines, characterised by their
angles $A^{(n)}$, $B^{(n)}$, $C^{(n)}$, and $D^{(n)}$.

A definite relation exists between these angles
and the position of the secant plane in space.
The latter may be defined by the spherical
co-ordinates " ω " and " ϕ," where ω is the angle
between the secant plane and the axial plane
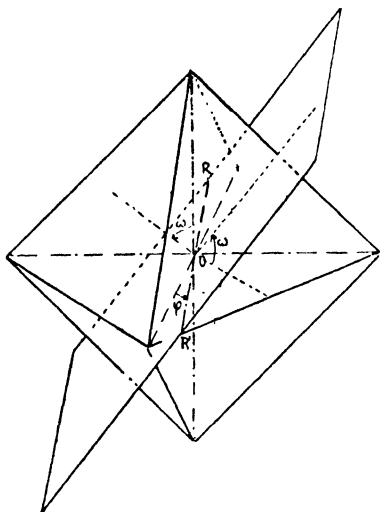
FIG. 22.—SAME AND A SECANT PLANE.

XOY (the angle between their normals) and ϕ
the angle between the axes OX and the section
of the planes XOY and the secant plane
(Fig. 22).

So the problem of defining the position in
space of a secant plane will resolve itself into
another one—that is, in finding the relation

existing between the angles A, B, C, and D on the one hand, and the angles ω and ϕ on the other. It may be mentioned that if the angles ω and ϕ are known, the position of the secant plane with regard to the axes of the octahedron is known too, as the axes of the crystal coincide with the axes of the co-ordinates.

The problem as thus stated has a great interest for crystallographers and metallographers, as it is the problem of determining the position of a section of a crystalline grain or grains and of the axes of the crystals.

The problem is somewhat complicated, as it involves numerous calculations. That is one of the reasons why, in spite of its interest, that problem never seemed very attractive to metallographers.

The author had the good fortune to secure the collaboration of Commander Dmitrieff, who, having an excellent mathematical training at his command, was not afraid of the difficulties and the tediousness of computation.

The results of his labours are given in a table where values of the angles A, B, C, and D are given as functions of the angles ω and ϕ. These values are given for every 5° of ϕ and for every 10° of ω (24).

Before proceeding any farther, it would be advisable to consider some particular cases; as, for instance, when the secant plane, running

TABLE I.—ANGLES A, B, C, and D = 180°—(A + B + C).

ω =	φ = 45°	40°	35°	30°	25°	20°	15°	10°	5°	0°
0°	90	90	90	90	90	90	90	90	90	90
	90	90	90	90	90	90	90	90	90	90
10°		1	3	4	5	6	7	8	9	10
	83	82	81	80	80	80	79	79	78	78
	14	14	14	14	13	13	12	12	11	10
	83	83	82	82	82	82	82	82	82	82
20°		3	6	8	11	14	16	18	20	21
	76	73	71	69	67	65	64	63	62	62
	28	28	27	27	26	25	25	24	23	21
	76	76	76	76	76	76	75	75	75	75
30°		6	11	16	20	24	27	30	32	34
	70	64	59	54	50	47	44	42	41	40
	39	39	39	39	38	37	37	36	35	34
	70	71	71	71	72	72	72	72	72	72
40°		12	22	29	36	40	43	45	47	48
	65	52	42	33	26	21	18	16	15	14
	49	49	49	49	49	49	49	49	49	48
	65	67	67	69	69	70	70	70	70	70
50°		37	54	56	52	53	51	50	49	48
	61	23	4	4	11	11	13	13	14	14
	57	57	57	53	49	47	47	47	47	48
	61	63	65	67	68	69	69	70	70	70
60°	58	56	53	50	46	45	42	39	36	34
	63	63	63	53	49	45	42	41	40	40
	58	19	1	11	17	22	25	28	31	34
		42	63	66	68	68	71	72	73	73
70°	56	52	49	43	39	37	33	29	25	21
	68	68	68	69	71	70	66	64	62	62
	56	41	26	14	6	2	8	14	17	21
		19	37	54	64	71	73	73	76	76
80°	55	50	45	39	33	29	24	20	15	10
	70	70	70	72	74	75	77	80	79	78
	55	45	35	26	18	12	5	0	5	10
		15	30	43	55	64	74	80	81	82
90°	55	54	41	34	27	21	16	10	5	
	70	70	70	72	74	76	77	82	85	90
	55	54	41	34	27	21	16	10	5	
		2	28	40	52	62	71	78	85	90

parallel to the face of either the cube or the octahedron, or the dodecahedron, reduces the number of different directions from four to two or three.

(*a*) $\omega = 0$. The secant plane is parallel to the axial plane. There are only two different sets of straight lines, and these, being perpendicular one to another, form squares and
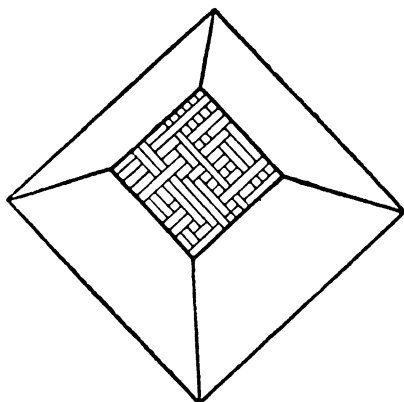
Fig. 23 —SECTION PARALLEL TO THE SURFACE OF A CUBE.
(After Tschermak, *Meteoritenkunde*, E. Cohen.)

rectangles. *This is the case of a section parallel to the surface of a cube* (Fig. 23).

If $\phi = 45°$ the secant plane bisects the angle between two octahedral axes ; two of the angles are equal, the third is $180° - 2A$; there are only *three* sets of lines and the figures seen on a section will be isosceles triangles.

(*b*) If in that case $\omega = \epsilon$ (half the angle

between two opposite faces, i.e. 54° 44′ 8″) all the three angles are equal, and the triangles become equilateral. *This occurs when the section is parallel to the surface of the octahedron* (Fig. 24).

(c) If ω = 90° then the secant plane comprises the vertical axes ; two of the sets of lines form the angle of 109° 28′ 16″. *This is the case*
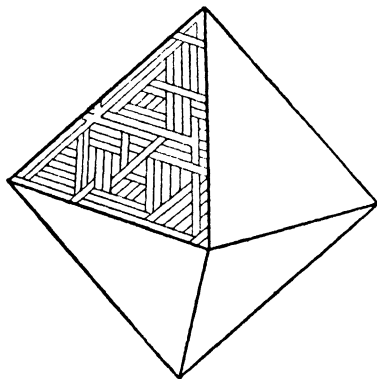
FIG. 24.—SECTION PARALLEL TO THE SURFACE OF AN OCTAHEDRON.
(After Tschermak, *Meteoritenkunde*, E. Cohen.)

of a section parallel to the surface of the dodecahedron (Fig. 25). Any other values of ω and ϕ will produce *four* sets of lines.

VIII. THE WIDMANSTÄTTEN STRUCTURE OF THE ALLOY No. 8

The various figures characteristic of the octahedral sections are familiar, to all who

study meteorites, under the name of *Widman-stätten figures.* Hence the Widmanstätten figures are a definite proof of octahedral crystallisation whenever they are present.

In 1909 the author read a paper before the Russian Mineralogical Society on the Widmanstätten structure in meteorites and terrestrial
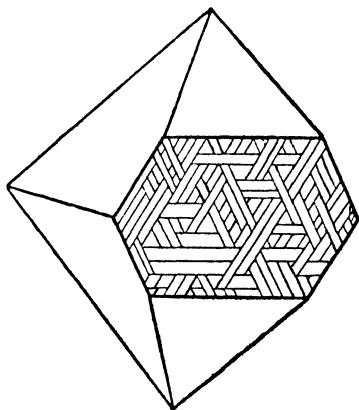
FIG. 25.—SECTION PARALLEL TO THE SURFACE OF A DODECAHEDRON.
(After Tschermak, *Meteoritenkunde*, E. Cohen.)

alloys (25). In that paper an alloy of 0·55% carbon with a perfectly developed Widmanstätten structure was described. The structure was macroscopic, perfectly discernible to the naked eye. A slight magnification of, say, x5, was, however, better to give all the details (Plate VII, Phot. 10, and Fig. 26).

On a section showing the general character of

the structure about twenty grains were shown, every one of them with sets of lines characteristic to that grain. It was easy to select pictures illustrating all the particular cases of the octahedral section—that is, a section parallel to the face of the cube, also to the face of the

Fig. 26.—WIDMANSTÄTTEN STRUCTURE OF THE ALLOY NO. 8 × 3.

octahedron, and to the face of the dodecahedron (Plate IX, Phots. 12 and 13).

These sections were reproduced side by side with the diagram of the octahedral sections, and so their similarity was made quite apparent.

In these particular cases it was easy to say

PLATE IX.—WIDMANSTÄTTEN STRUCTURE.
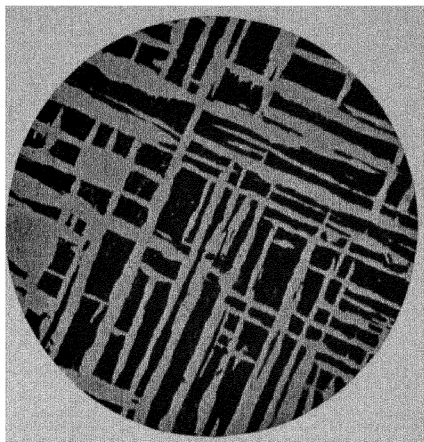
Phot. 12.—SECTION PARALLEL TO THE SURFACE OF A CUBE.
Alloy No. 8— × 30.
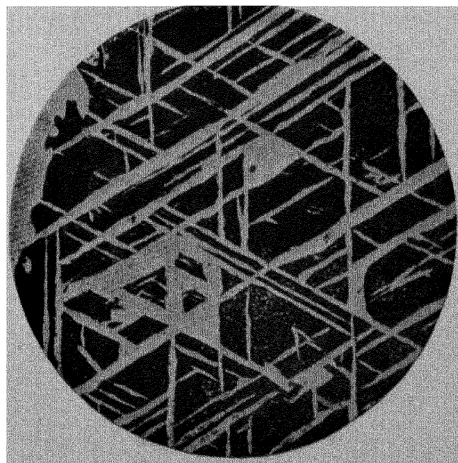
Phot. 13.—SECTION PARALLEL TO THE SURFACE OF AN OCTAHEDRON.
Alloy No. 8— × 30.

how the section of the slide was placed with
regard to the axes of the octahedron, but such
characteristic cases occur comparatively seldom.
For instance, on the section referred to above,
out of twenty grains only in one case (grain No.
VIII) occurred two directions, and in two cases
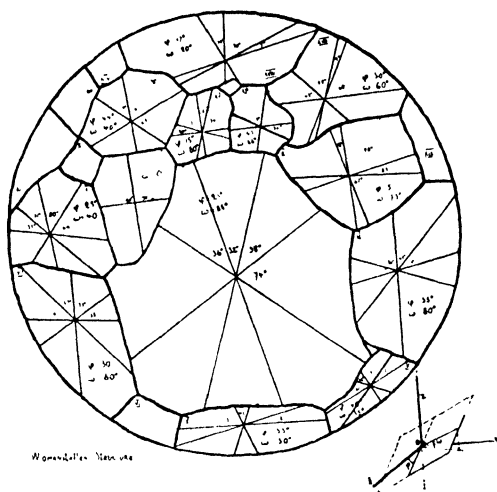
FIG. 27.—DIAGRAM OF THE GRAINS OF THE ALLOY NO. 8.

(Nos. XII and XVI) three ; in all other grains
there are four directions and the position cannot
be determined *without special calculations or
reference to the above-mentioned table.*

Commander Dmitrieff has calculated the ω's
and φ's for all these grains but seven (where the
lines were too confused to allow of any accuracy

of measurement). The results are given in Table II, and on Fig. 27.

TABLE II

NN	A	B	C	D	Number of Direction.	ϕ	ω	Remarks.
I	36°	32°	38°	74°	4	25°	85	
II	12	78	23	67	4	5	73	
III	35	70	45	30	4	35	80	
IV	61	42	65	12	4	40	35	
V	71	42	55	12	4	35	30	
VI	—	—	—	—	4	—	—	Lines indistinct.
VII	45	27	73	38	4	30	80	
VIII	90	0	90	0	2	0	0°	Parallel to the face of the cube.
IX	35	31	50	64	4	25	40	
X	—	—	—	—	4	—	—	
XI	—	—	—	—	4	—	—	Confused.
XII	49	63	68	0	3	44	40	Close to face of octahedron.
XIII	—	—	—	—	4	—	—	Confused.
XIV	—	—	—	—	4	—	—	Confused.
XV	20	71	15	74	4	44	40	
XVI	73	73	34	0	3	45	25	
XVII	48	55	9	68	4	30	60	
XVIII	73	30	70	7	4	17	80	
XIX	—	—	—	—	4	—	—	
XX	—	—	—	—	4	—	—	

There are many questions which present themselves once such data is available ; for instance, is there any relation between the axial planes of neighbouring grains or between the surrounding grains and the central one ? or is the orientation of various grains, as is usually supposed, independent one of the other ?

Addressing, some time ago, the London Section of the Institute of Metals on the question of the structure of the grain (24), the author

expressed the opinion that when a large number of slides suitable for such measurements are prepared and taken advantage of our knowledge will considerably increase, but that meanwhile he would say that certain values of ϕ on his particular section seem to occur more frequently than others. This observation may possibly lead to some further investigations. That is all that can be said now without seeming rashness.

Another valuable application would be to compute the angles in the case of strained materials. Then we could know how the direction of stress lies with reference to the axial planes. He would also like to say that the beautiful samples of aluminium prepared by Professor Carpenter might be tested by that method.

But however interesting these and like considerations are, they point to a side issue. *The main fact is that by that method the structure of the crystalline matter in every grain and the orientation of one grain with reference to another is made perfectly intelligible and accessible to direct measurement.*

IX. WIDMANSTÄTTEN FIGURES IN METEORITES —SYNTHETIC REPRODUCTION OF THIS STRUCTURE IN THE IRON CARBON ALLOYS.

Meteoric Iron or Siderites consist chiefly of iron and nickel. The iron content varies from

80 to 94%, and the nickel from 6 to 10%. The other elements usually present in steels, as sulphur, phosphor, carbon, and silicium, are also found in siderites.

The chemical composition of meteorites does not present anything which would attract our attention. Such steels in the constitutional diagram of terrestrial nickel steel would be considered as pearlite steels, just on the border of martensitic steels. The more striking, therefore, is their structure and their metallographic components.

Such of the siderites as are poor in nickel, containing less than 6 or 7%, show cleavages parallel to the face of the cube, and are called *Cubic Irons,* or hexahedrites.

Those richer in nickel are called *Octahedral Irons,* or octahedrites. They show, on etching, Widmanstätten figures in lamellæ of three constituents—*camacite, taenite,* and *plessite*— are arranged parallel to the faces of the octahedron.

Camacite may be considered as a solid solution of 0·7% of nickel in iron, or as a nickel-ferrite ; *Taenite* as a solid solution of 0 to 50% of iron in nickel ; *Plessite* (about 40% of nickel) as their eutectoid, and analogous to pearlite in the iron-carbon alloys.

Not one of these constituents was ever found in the terrestrial iron-nickel alloys, and this

disintegration was considered for a very long time as a great puzzle.

Another puzzle was the so-called *Widmanstätten* figures. They were first investigated in 1808 on the Agram Iron by Alois de Widmanstätten, the Director of the Imperial Porcelain Works at Vienna. Widmanstätten did not publish the results of his discovery, but the knowledge spread very quickly, and quite shortly the figures became known as " Widmanstätten figures." Very soon crystallographers found out their relation to the octahedral sections, but it was generally considered that these figures were characteristic of meteoric iron and that they were not found in terrestrial iron (26). So metallographers up to the end of the last century do not seem to have been acquainted with them.

The interest shown in meteorites by Dr. Sorby, the founder of the Science of Metallography, and especially the brilliant researches of Osmond, again, however, directed attention to the figures of Widmanstätten. Thus, in 1900 Osmond announced the discovery in the head of a steel ingot of equilateral triangles, " recalling," he said, " the figures of Widmanstätten, which are known to belong to the regular octahedral system " (27).

The same observation was made in 1905 by Professors Arnold and McWilliam in their

paper on *Thermal Transformation of Carbon Steel* (28).

In 1908, when the author was trying to reproduce the " Damascene " structure, and was very much engrossed in that problem, hoping to be able to discover at the same time a pearlite discernible to the naked eye, he received from the Ijevsky Works the Alloy No. 8, with 0·55% of carbon, prepared in accordance with his directions.

It took some time for the author to realise that the first synthetic production of Widmanstätten figures was in his hands.

The analogy between the structure of that alloy and that of certain octahedrites was so close, the relation of figures seen on a section to the crystallography of the grain so striking (Plate X, Phots. 14 and 15), that the author considered himself justified in placing such a structure in a separate class of secondary structures, and call it, in honour of A. Widmanstätten, the *Widmanstätten Structure* (29).

In a later paper the author drew attention to the great extent to which Widmanstätten structure exists in different alloys and metals (30).

So, not only could the meteoritic structure be henceforth artificially reproduced at will, but the relation between the meteoritic and terrestrial structures be established. as well as their crystallographic character.

PLATE X.—WIDMANSTATTEN STRUCTURE IN STEEL
AND IN METEORITES.
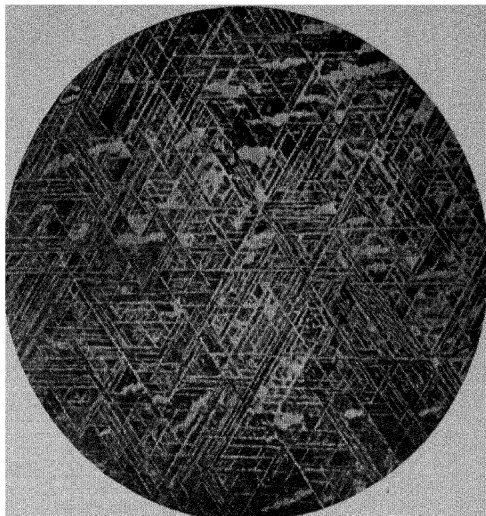
Phot. 14.—SECTION PARALLEL TO THE SURFACE OF AN OCTAHEDRON.
Alloy No. 8 – × 9.
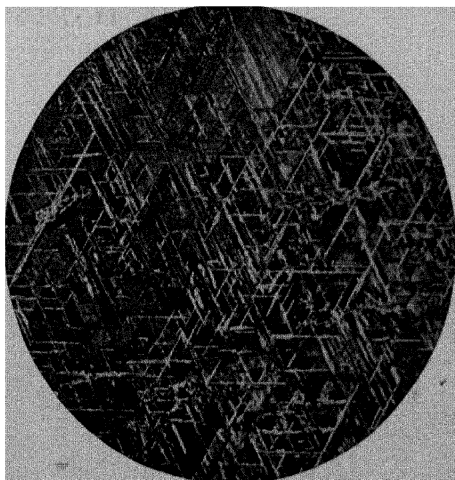
Phot. 15. SAME IN THE TAZEWELL METEORITE.

X. SYNTHETIC REPRODUCTION OF THE METEORITIC STRUCTURE IN ALLOYS OF IRON AND NICKEL

There remained, however, one last step to be made, namely, to reproduce the meteoritic structure in iron-nickel alloys of similar composition. This last crowning effort was accomplished with great success in 1910 by Dr. Carl Benedicks in Upsala, Sweden.

But here again we have to mention first the name of Osmond, which name is always met with in metallography as soon as a new path is to be traversed.

In 1904, in a paper on *Meteoric Irons* (31) Osmond, in conjunction with Cartaud, worked out a diagram of iron and nickel when *cooled* extremely slowly.

According to that diagram the secondary crystallisation, manifesting itself in the throwing out of either *camacite* or *taenite,* would have started at temperatures of about 800° C. for the former and 600° for the latter and would end at about 360° by the formation of the eutectoid plessite. Thus, a complete analogy between the process of secondary crystallisation in iron-carbon alloys and meteorites was suggested (32).

It was also implied that above these temperatures the solid solution was in the gamma or octahedral state, and that only below the cubic

modification occurred. The question of the primary dendritic crystallisation was not detailed.

Dr. Carl Benedicks conceived the idea of suppressing the possible dendritic crystallisation by a first rapid cooling from the melt (from about 3,000°), then to bring it again in the gamma zone (a possible granulation zone) and then to let the alloy cool as slowly as possible through the area of secondary crystallisation and the eutectoid zone.

His insight was rewarded by a brilliant success, as in his second melt he was able to obtain a large amount of plessite. Subsequently, camacite was also obtained, as well as a fine and distinct Widmanstätten structure (33).

So the problem which has been tackled by such distinguished scientists as Stodart and Faraday, Daubrée, Meunier, and even Sorby, was finally solved (34).

The structure of meteoric irons is no more a mystery to us, but in solving that mystery the meteorites seemed to bring to us a message causing us to know and understand that the same laws govern the synthesis and crystallisation of matter both here on our earth, and there in the vast infinite space whence the meteorites come.

*

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Lecture III

CRYSTALLISATION OF EUTECTICS AND EUTECTOIDS

CONTENTS

LECTURE III

CRYSTALLISATION OF EUTECTICS AND EUTECTOIDS

I. INTRODUCTION

THE constancy of the temperature of fusion is considered in chemistry as one of the most important properties of a definite chemical compound. This property is shared by chemical compounds with pure substances and provides a suitable demarcation line between a " chemical " compound and a " mechanical " aggregate.

There is, however, one notable exception, and that is the case of the so-called " Eutectic " mixtures, or in metals, of " Eutectic Alloys."

A eutectic mixture, or " eutectic," is the portion of the mother liquor (or of the alloy) to solidify last ; its structure is that of minute particles of the components. It is therefore an " aggregate." Nevertheless, its freezing or melting temperature is constant and one and the same. The constancy of the freezing temperature and the minuteness of structure for a long

time made the confusion of eutectics and chemical compounds most natural. For instance, Guthrie, who was the first to study the eutectic mixture of water and salt, considered it as a definite compound, but stable only at low temperatures. He called it therefore a " cryohydrate " (35).

Subsequently the structures of that and other cryohydrates were shown to be one—a mechanical aggregate of minute particles of the components (36).

The study of metallic alloys has furnished many examples of analogous mixtures, and their properties and structure have been investigated in all details. So it has become established that such mixtures have a constant composition, freeze at a constant temperature, and, moreover, that their temperature of freezing is the lowest. Hence their name " eutectics " which means " easily melting " (37).

Let us take, for instance, the case of the alloys of lead and antimony (38). The freezing point of lead is 326°, that of antimony 632°. The composition of the eutectic alloy is 12% of antimony and 88% of lead. The temperature of freezing of that alloy, or the *eutectic temperature*, is 228°. That temperature is the lowest freezing temperature for any alloy of lead and antimony. An addition of either of them to the eutectic would cause the freezing to start at a

higher temperature, the completion of solidifica-
tion always occurring at the constant eutectic
temperature (Fig. 28).

The structure of this eutectic will be that of an
aggregate of minute particles of lead and anti-
mony. An alloy of such composition will
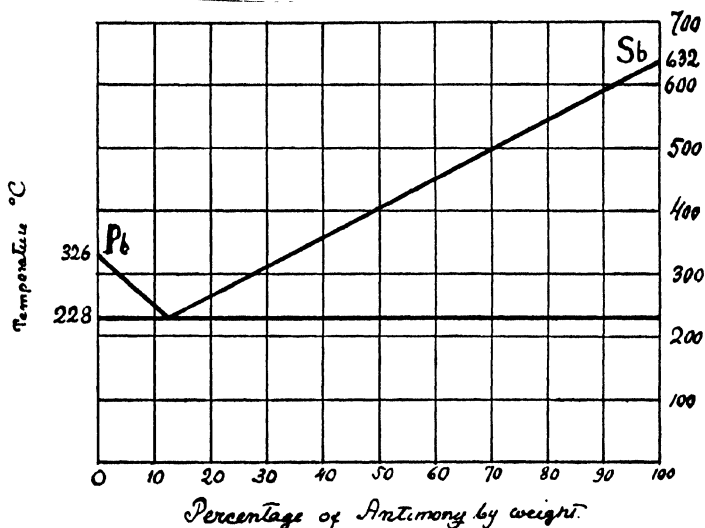

FIG. 28.—FUSIBILITY CURVE OF ALLOYS OF LEAD AND ANTIMONY (Roland-Gosselin).

consist of the eutectic only. In an alloy of
less than 12% of antimony, or a hypo-eutectic
alloy, crystals of lead will be added ; in a hyper-
eutectic alloy, crystals of antimony.

Whenever two metals are insoluble in each
other, analogous types of structure would
appear. In every alloy a certain amount of

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eutectic would occur. Therefore such alloys are called *Eutectiferous alloys.* A classical case is that of silver-copper, investigated by Osmond with a eutectic of 28% of copper and 72% of silver (39). Alloys of iron and carbon, bronzes and brasses, to cite a few cases only, all belong to the eutectiferous alloys (40).

II. The Structure of Eutectics—General Considerations

The constancy of the temperature of freezing of a eutectic may be easily demonstrated by the so-called " phase rule " (41).

In its simplest form the " phase rule " is generally expressed by the formula :

$$F = n + 1 - P$$

where by " F " is denoted the so-called " degree of freedom " of a system with reference to temperature and concentration, by " n " the number of components, and by " P " the number of phases.[1]

---

[1] By the " phases " of a system are meant " the homogeneous, physically distinguishable, and mechanically separable constituents of a system " (Sauveur).

By " components " are meant " entities which are undecomposable under the conditions of the experiment " (Mellor).

By the " degrees of freedom " are meant the number of the independently variable factors, temperature, pressure, and concentration which affect the constitution of the system. In the case of the alloys the influence of pressure is usually ignored.

The phase rule in that form implies that *when a system is in a complete equilibrium* the degree of freedom equals the number of components plus one and minus the number of phases present, or, in other words, *show how many phases can be present at one time under given conditions*.

For a binary alloy $n = 2$, thus

$$F = 3 - P.$$

As one phase at least is necessary the maximum degree of freedom of a binary system will be 2 and the equilibrium will be called *bivariant*.

In the case of two phases the degree of freedom will be reduced to *one* and the system become *monovariant*.

If three phases are present simultaneously the degree of freedom becomes nil, and the system is called *nonvariant*.

Let us take a system of points the co-ordinates of which are x and y. If both x and y vary *independently* and *unconditionally* between $+ \infty$ and $- \infty$ every point on a plane will be obtained. If there are some limiting conditions, for instance $x > a$ or $y < b$, only a certain limited area will be obtained. As the degree of freedom of such a system is 2, we can say that a bivariant equilibrium will be represented by a certain area.

Let us now take the equation

$$y = f(x)$$

and assume that x varies independently, whereas y is its function.

The locus of this equation is a line and the degree of freedom is one. Therefore we may say that a monovariant equilibrium is represented by a line.

Let us further take a certain pair of values for x and y. To such a pair in all the plane corresponds one and only one point. There is no freedom in such system at all, in other words, the degree of freedom equals zero.

Let us take again the formula of the phase rule,

$$F = 3 - P$$

If $F = O$ then $P = 3$. This means that in a binary system not more than three phases can exist simultaneously. Moreover if three phases are present, the system becomes nonvariant and can exist at one definite temperature and concentration only. Such a nonvariant equilibrium is necessarily unstable.

Let us take a binary system—for instance, that of lead and antimony. At the eutectic point the liquid phase is in equilibrium with two solid phases, the solid crystals of lead and of antimony. The system is nonvariant, the composition or concentration is the constant one of 12% antimony and 78% lead ; the temperature is also constant and is the eutectic temperature of 228°.

The solidification of an alloy of eutectic composition will proceed at that constant temperature until the whole will become solidified, just as in the case of definite compounds. Still, after solidification, the eutectic alloy will consist of juxtaposed particles of both components.

The structure of these varies in different eutectics. Sometimes the particles are like scales or lamellæ, sometimes like small spheres or globules, sometimes they have a crystalline appearance. In every case, however, they are exceedingly minute and the structure of a metallic eutectic is usually resolved under the microscope only.

III. The Process of Crystallisation of a Eutectic

Let A and B be two metals insoluble one in another in the solid state. Let temperatures be plotted as ordinates and the percentage composition as abscissæ. Let the point E denote the eutectic point. Let AE be the temperatures of the beginning of solidification or the "liquidus" of hypo-eutectic alloys, and BE the liquidus for hyper-eutectic alloys. The solidification will end "on the line CD" (or "Solidus" line) at the constant eutectic temperatures.

Such a diagram is called the "Equilibrium"

or " Constitutional " diagram of a binary system, as it shows the constitution of a binary alloy of any composition at various temperatures, *if and when equilibrium was attained.*

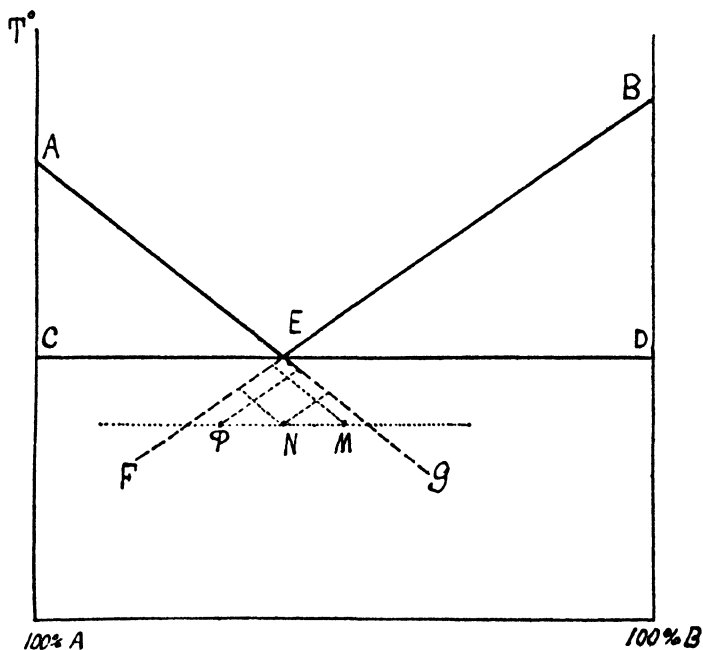In other words, the diagram may serve as an

FIG. 29.—EQUILIBRIUM DIAGRAM OF A BINARY SYSTEM.

indication of the ideal constitution of an alloy when all " phases " are in equilibrium.

Under such *ideal* conditions a hypo-eutectic alloy would begin to solidify exactly " on the line " AE, i.e. on temperatures represented by

that line, a hyper-eutectic alloy on the line EB and an alloy of eutectic composition as soon as the temperature has reached the " eutectic temperature " value.

Actually, the process of solidification even when the cooling is slow and undisturbed would not exactly comply with the diagram.

Every alloy, before solidification starts, will be brought a little beneath the transformation line, or, in other words, " undercooled." So, for instance, a hyper-eutectic alloy will be brought beneath the line BE, the hypo-eutectic alloy below AE, and the eutectic alloy beneath CD.

As, under ideal equilibrium conditions, the crystallisation of the component A starts on the line AE, and the crystallisation of B on the line BE, undercooled alloys will be also super-saturated, those to the left of AE with regard to A and those to the right of BE to B.

Let us now consider more closely the case of an alloy of eutectic composition. Such an alloy if undercooled would be brought beneath the line CED. As the dotted lines EG and EF show, the alloy will be to the right of EB and simultaneously to the left of AE ; that is to say, *an undercooled eutectic alloy will be supersaturated simultaneously with regard to both components.*

As in fact a certain degree of undercooling is necessary to start every process of solidification,

every eutectic crystallisation will start in an alloy supersaturated with regard to both components. Let, for instance, N be the figurative point of an undercooled alloy of eutectic composition just before crystallisation starts. Let us assume that a certain amount of A has crystallised out first. The figurative point will move from N to M and supersaturation with regard to B will only have increased. Therefore, the next immediate step will be that of throwing out a corresponding amount of B. Then, oscillating between the two, the whole mass of eutectic composition will undergo the transformation and finally resolve itself into alternate layers of the two constituents A and B.

IV. The Structure of a Lamellar Eutectic

What will be the influence of eutectic crystallisation on the size and the shape of the particles? Actual observation shows that usually the *size* of the particles is extremely minute and their shape varies from the characteristic lamellæ or " scales " through intermediary stages (like, for instance, bunches of rods) to globules and spherolites.

It is important to note that whatever their shape, the particles usually seem to be arranged in regular groups, in every group running parallel to a definite plane, thus suggesting the

" granulation " of the eutectic into a certain number of *crystalline grains.*

The different orientation of the particles in different grains is clearly shown, for instance, by Desch in a eutectic alloy of bismuth and tin (42) ; the same phenomenon is also very apparent in the grains of pearlite. Whenever the composition of the alloy is close to the eutectic—that is to say, in the absence of any " excess " elements—the distribution and general character of particles tend to become as just described. On the other hand, the occurrence of large masses of previous deposits changes the aspect and distribution of the particles, causing a certain " branching off " and distortion of the general picture.

Let us assume that an alloy of eutectic composition cools down very slowly, that the process of eutectic crystallisation results in the formation of grains of eutectic, that the undercooling is considerable. It has been demonstrated in several instances that the greater the undercooling the more sudden is the crystallisation, and consequently the greater the probability of the deposit to be forced to lodge itself parallel to some already existent or perhaps " potential " crystallographic plane. The most suitable shape for such deposit would be that of a thin film or scale. We may further imagine that such a film would stretch through the whole grain from

one boundary to another. This first deposit will be followed by a similar one, but of the second component, and so on in rapid succession until the whole of the mass has crystallised.

Sir George Beilby in the *Aggregation and Flow of Solids* (43) furnishes us with a very interesting instance of formation of aggregates of silver chloride from dilute solution of silver nitrate and sodium chloride. He narrates how the first visible step is the formation of an extremely thin film, and how in that film the first formations are to be detected, the formation being " not spheres, but minute plates or scales."

As the precipitate is absolutely insoluble, the reaction must follow its course until the whole of the silver chloride has been deposited. There is therefore a certain " outer " analogy with the nonvariant process of the formation of eutectics. In the former case, as soon as the two drops of diluted liquids meet, a *thin film* of the precipitate is formed on the common surface, and if broken up is immediately replaced by a fresh one ; in the latter, as soon as the process starts, thin films of the first deposit are thrown out and immediately followed by analogous films of the other components. In both cases the films are metastable, and would tend to alter their shape as soon as possible ; so, for instance, in the case of salts, they can only be detected for a brief moment. In metals, however, they can exist

for a very long period and special heat treatment may be needed to produce what is called " the structural equilibrium."

However, the analogy with the formation of salts may strengthen our belief that the conditions of the nonvariant eutectic transformation are best translated into the metastable structure of lamellar eutectic.

V. THE CRYSTALLISATION OF PEARLITE

Let us suppose that a process is going on in a solid, which results in a decomposition of a solid phase, and in a subsequent throwing out of two new phases ; for instance, the already referred to process of secondary crystallisation in steel, where the solid solution or austenite is being gradually decomposed into two new phases, cementite and ferrite. As already mentioned, at a temperature of 690°, which is the lowest of all the transformation temperatures, the residual alloy with 0·85% of carbon is bodily transformed into pearlite. Like eutectics, pearlite consists of minute particles of both constituents (44), its chemical composition or " concentration " is constant, and the temperature of the process is constant also. In view of such a complete analogy with eutectics pearlite and similar constituents are called " eutectoids " (45).

The eutectoid process is also nonvariant ; al

the general considerations applied to eutectics are also applicable to eutectoids, and vice versa.

There is strong evidence in support of the " granulation " hypothesis of eutectics in the case of pearlite (46). It is common knowledge,
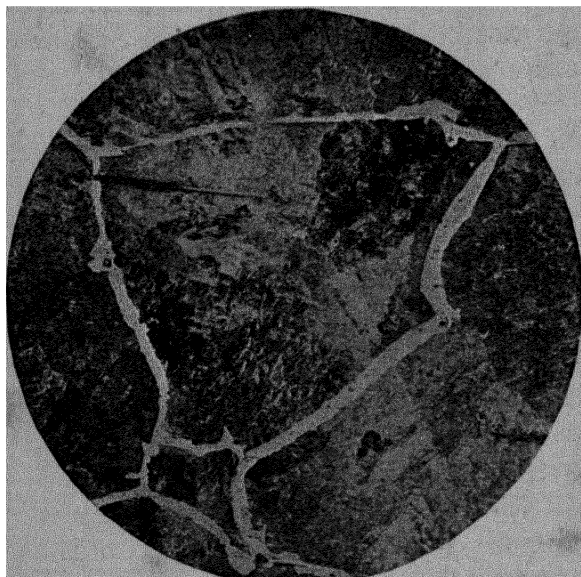
FIG. 30.—PEARLITE GRAINS INSIDE A FERRITE MESH
(a former gamma grain).
Alloy No. 5—C = 0·60%—× 40.

for instance, that the small light and dark areas seen in pearlite under low magnification are exactly like crystalline grains in metals, and may therefore be described as " pearlite grains " (Fig. 30 and Plate XI, Phot. 16).

It seems very likely also that the process of

PLATE XI.—PEARLITE

PHOT. 16.—"PEARLITE GRAINS" AND "FREE" FERRITE.

PHOT. 17. *Vide* PHOT. 16.—THE STRUCTURE OF PEARLITE.
× 300.

granulation or of the formation of pearlite grains proceeds exactly on the same lines as already indicated for metals—that is to say, that nuclei are formed and from these the crystallographic rearrangement proceeds with a certain linear velocity. In this way, in the original gamma iron mass, new alpha grains are built up. Simultaneously with that rearrangement,
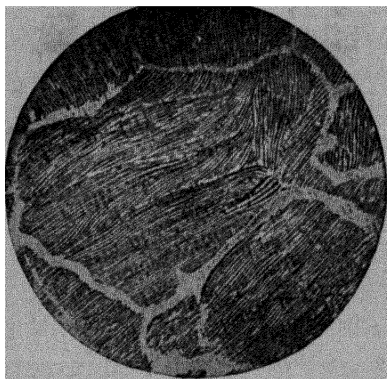
FIG. 31.—PEARLITE (SORBY).
(Sauveur, *Metallography*, fig. 145.)

cementite lamellæ are thrown out and the formation of pearlite goes apace.

At a higher magnification the inner structure of every pearlite grain becomes apparent (Plate XI, Phot. 17). That structure was first described by Sorby (44) and we reproduce from A. Sauveur's *Metallography* one of Sorby's early drawings of pearlite (Fig. 31). The accuracy and beauty of it are remarkable.

As is usually the case with secondary deposits in an already crystallised mass, the lamellæ of cementite will lodge themselves parallel to the crystallographic plane of the earlier deposits, in that case of the alpha grain.

As alpha iron crystallises in cubes we may assume that the lamellæ will arrange themselves parallel to the faces of the cube. The first lamella " selects " one of the faces, the others follow suit. Let us imagine two dissimilar packs of cards in a square-sided box. This will illustrate the " packing " of lamellæ of cementite and ferrite in a pearlite grain.

It is important to note that such " variously oriented " packs of cementite and pearlite lamellæ constitute the whole mass of the pearlite of an alloy. Therefore what we see on a photo-micrograph is the picture of one of the sections only. As that which is of real importance is the arrangement *in space*, we come to the same problem as we meet in the case of Widman-stätten structure—namely, to define the stereo-metric relations of various deposits on the basis of their traces on various sections.

VI. STEREOMETRY OF AN IDEALISED PEARLITE GRAIN

The shape of a pearlite grain, like the shape of every metal grain, will depend on the conditions

of cooling through the transformation area and on the properties of the crystallising matter. This shape will be that of a more or less regular polyhedron.

Inside every grain the lamellæ of cementite and pearlite will be arranged in alternate layers, roughly parallel one to another and to a face of a cube.
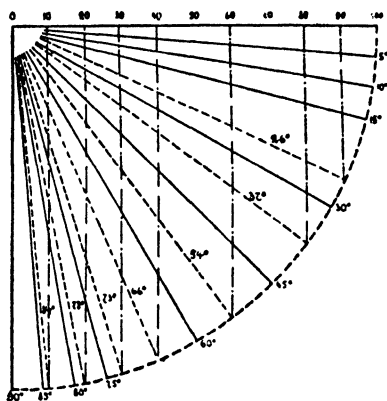
FIG. 32.—A QUADRANT SECTION OF AN IDEAL PEARLITE GRAIN.

If the section is normal to that face all the lamellæ will be seen as so many parallel lines. If, on the contrary, the section runs parallel to that face only one lamella will be seen. Between these extreme cases there are many intermediate.

Let us assume that a sphere is inscribed in a polyhedral pearlite grain. Let the total number of cementite lamellæ be 200. A quadrant section

perpendicular to the lamellæ will show all the lamellæ of one quadrant, i.e. 100 (Fig. 32).

The picture will be that of idealised lamellar pearlite (Fig. 33).

Let us consider a section inclined to the normal plane at 26°. As Fig. 32 shows, ninety instead of one hundred lamellæ will appear. The apparent thickness and the distance between the
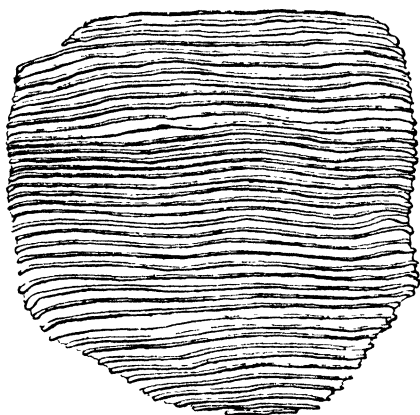
FIG. 33.—A DRAWING OF A SECTION, ω = 0°.

lamellæ slightly increase, but the pearlite will still have the same appearance. Consecutive sections at 37°, 45°, and 54° will respectively show 80%, 70%, and 60% of all the lamellæ. A section at an angle of inclination (ω) of 60° will show 50% of lamellæ, the distance between them increasing in the ratio of two to one. Still the character of the grain will remain much the same and the " pearlite " will seem only less

closely packed. The next sections at 66°, 73°, and 78° begin to look rather " coarse."

Lastly, a section inclined at an angle of 84° will show only 10% of lamellæ, and at 87° only 5%. The width of lamellæ and their apparent distances will in the last sections increase ten times for the former and twenty times for the latter.
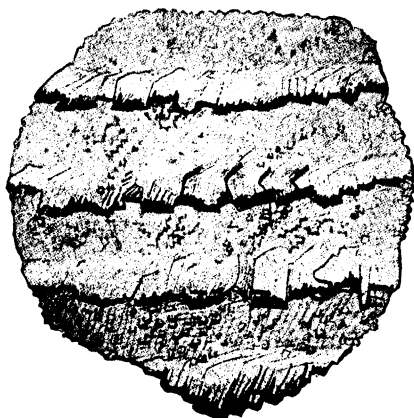
FIG. 34.—A DRAWING OF A SECTION, ω = 84°.

Such increase must necessarily bring about a great change in the appearance of the lamellæ on actual slides. Let us first consider two diagrams drawn from " life "—that is to say, from actual grains—the one at an angle of inclination zero (Fig. 33) the other of 84° (Fig. 34). Let the whole number of lamellæ be 40. All these will be seen on the first, and only 4 on the second.

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These two diagrams show how simple " stereo-metric " relations may entirely alter the familiar aspect of the pearlite grain. They also show how the angle of inclination (ω) of the section to the face of the cube may be computed from the number of cementite lamellæ in a grain (N), or from their apparent distances ($\triangle$).

These questions present a fascinating study in themselves, and have formed the subject of a paper presented to the Spring Meeting of the Iron and Steel Institute (47).

VII. The Structure of Pearlite on Various Sections

Let us examine the pearlite area of the alloys of hyper, hypo, and eutectoid steels prepared by the author. All these alloys were prepared under conditions of slow and undisturbed cooling, and in every case an undercooling was expected and a lamellar pearlite obtained.

For the purpose of investigation three alloys were selected, the Alloy No. 1 with 1·80% of carbon, the No. 21 of eutectoid composition, and No. 8 with 0·55% carbon, so that pearlite of the eutectoid steel might have been compared with the pearlite of the other two.

The structure and general distribution of lamellæ of cementite in various grains was found to be the same, and governed by the same laws ;

PLATE XII.
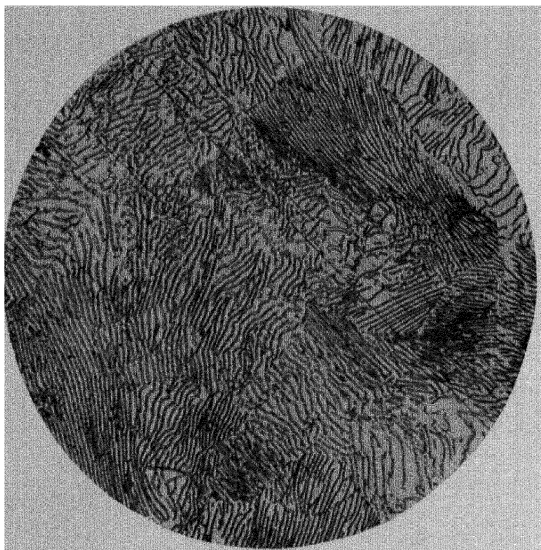
Alloy No. 1— × 250.
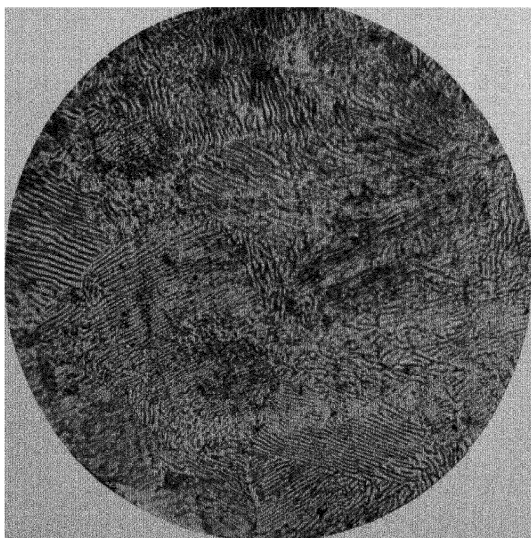
PHOT. 19.—PEARLITE.
Alloy No. 8 — × 1,000.

the " coarseness " was found to be different. It seems as if the coarseness depended on the general character of the structure, the pearlite of the Alloy No. 1 with the structure of large crystals and of hyper-eutectoid composition being about four times as coarse as the pearlite of the eutectoid and hypo-eutectoid alloys with Widmanstätten structure. On the other hand, the coarseness of the Pearlite No. 1 was exactly the same as that of the hypo-eutectoid Alloy No. 5 with 0·60% carbon and network structure.

So the coarseness of pearlite seems to depend not on the carbon content but on the velocity of cooling through the transformation range (Ar_1).

As just mentioned, the pearlite of the Alloy No. 1 is about four times coarser than that of Nos. 8 and 21. Therefore, a section of one of the latter at a magnification of 1,000 would appear like a section of the Alloy No. 1 at 250 (Plate XII, Phots. 18 and 19). As the general character and the change in the number of lamellæ in neighbouring grains are the same, we may assume that the reason for that change is the one suggested—namely, the difference of the angle under which various grains appear on a section.

Let us examine now more closely sections of various grains of the alloys. The angle of inclination, as computed from the distance

between the lamellæ, varies within large limits, in some of the grains being as much as 78° (Plate XIII, Phot. 20), 80° (Plate XIV, Phot. 21), 82° (Plate XV, Phot. 24), and even 86° (Plate XVI, Phots. 25 and 26).

It is interesting to note what an immense change occurs in the aspect of the cementite lamellæ at such angles—some of them seem quite ragged ·and distorted—just an anticline thoroughly weathered out (Plate XIV, Phot. 22, and Plate XV, Phot. 24).

The analogy indeed is not only apparent, but very real. In both cases layers of substances of various resistance " to wear " are subjected to the disintegrating influence of acidulated water and other agents. In one case it is caused by the " general economy " of nature, in the other by the grinding, polishing, and etching processes.

As a result the less-resistant layers give way more, in our case ferrite, and form the background ; the harder and more resistant, like cementite, or, say, igneous rocks, stand out in relief as so many ribs, but still offer a ragged appearance.

Some of the cementite lamellæ are extremely instructive from this point of view, as on broken edges the crystallography of cementite is perfectly brought into evidence (Plate XVI, Phot. 25). One must realise the extreme minuteness

PLATE XIII.
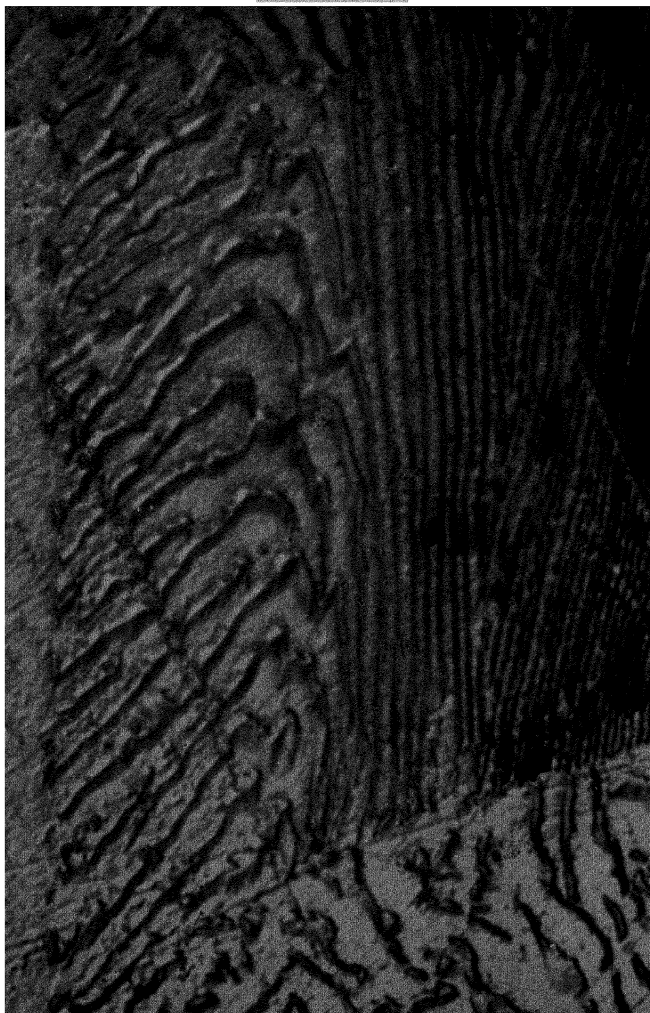
PHOT. 20 PEARLITE
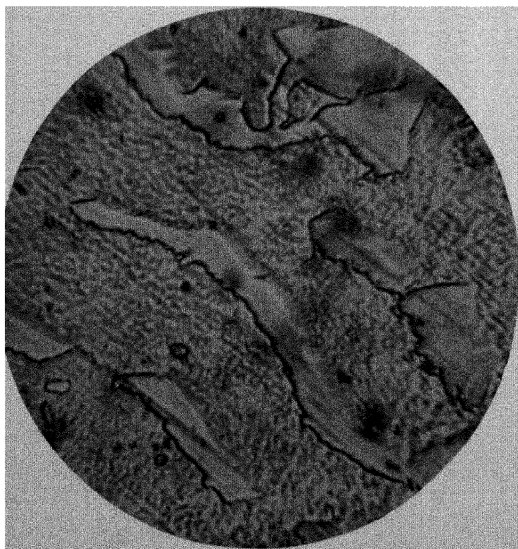(B. Brandt in the Author's Laboratory)
Alloy No. 8—ω - 78°   × 500

PLATE XIV.

PHOT. 21.— $\omega = 80°$ - Alloy No. 8— × 2,000.

PHOT. 22.— $\omega = 83°$—Alloy No. 1— × 2,000.
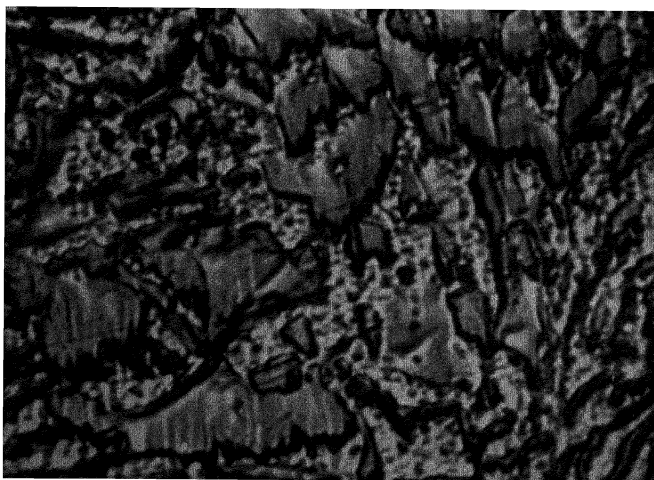(B. Brandt in the Author's Laboratory.)

PLATE XV.

PLATE XVI

PHOT. 24.—Alloy No. 21—ω = 86°— × 2400.

PHOT. 25. Alloy No. 21 ω ?— × 3000
(B. Brandt in the Authea's Laboratory.)

of these exceedingly thin lamellæ, which are seldom thicker than half a micron (48), to appreciate the exact likeness of the processes of geological formations and that of the pearlite grain.

The difference in scale is stupendous, the likeness in character and even in substance not less so. And again the same conclusion on the general applicability of the same laws in macro- and microcosm is irresistibly forced upon us.

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37. *On Eutexia.* By Dr. F. Guthrie. " Phil. Mag.," June 1884, p. 462. See also :

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Microscopic Study of Metallic Alloys. By G. Charpy. Bul. Société d'Encouragement pour l'Industrie Nationale," March 1897, and " Metallographist," 1898, Vol. I, pp. 87–106 and pp. 192–209 (p. 91).

38. The curve of fusibility of the Alloys of Lead and Antimony was first determined by Roland-Gosselin and subsequently confirmed by Charpy (" Metallographist," 1898, p. 95) and Stead (" Metallographist," 1898, p. 179).

39. " Metallographist," 1898, pp. 5–27 (p. 15).
    The curve of fusibility of the Alloys of Silver and Copper was first constructed in 1875 by Roberts Austen and subsequently by Heycock and Neville.

40. *The Constitution of Steel considered as an Alloy of Iron and Carbon.* By A. Sauveur. " Technology Quarterly," June 1898, Boston, U.S.A., and " The Metallographist," 1898, pp. 210–229 and (37).

41. J. W. Gibbs. " Trans. Conn. Acad.," III, 116, 1875, and " The Scientific Papers of J. W. Gibbs," London, I, 55, 1906, quoted from J. W. Mellor, " Inorganic and Theoretical Chemistry," Vol. I, p. 450.
    With special reference to the Iron-carbon System, see :

    (*a*) A. Sauveur. *The Microstructure of Steel and the Current Theories of Hardening,* " Transactions American Institute Mining Engineers," 1896, p. 867, where the first Iron-carbon Diagram was published.

    (*b*) Roberts Austen. *Fourth Report to the Alloys Research Committee,* Institution of Mechanical Engineers, 1897.

    (*c*) Roberts Austen. *Fifth Report,* and " Metallographist," 1899, p. 186.

    (*d*) *Iron and Steel from the Point of View of the Phase Doctrine.* By Bakhius Roozeboom. " The Metallographist," 1900, p. 293, and " Zeitschrift fur physikalishe Chemie," XXXIV, 1900.

    (*e*) *Iron and Steel from the Point of View of the Phase Doctrine.* By F. Osmond. " Metallographist," 1901, p. 150.

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    (*g*) *The Range of Solidification and the Critical Ranges of Iron-Carbon Alloys.* By H. C. H. Carpenter and

B. F. S. Keeling. "The Journal of the Iron and Steel Inst.," 1904, and "The Iron and Steel Magazine" ("Metallographist"), Vol. VII, 1904, p. 628, where the various lines of the diagram were experimented, checked, and finally established.

The famous Tschernoff Diagram, published as long ago as 1868, furnishes all the data for the left side of the diagram.

42. *Metallography.* By C. Desch. Eutectic Alloy of Bismuth and Tin.

43. *Aggregation and Flow of Solids.* By Sir George Beilby. London, 1921, pp. 52–54.

44. *Pearlite*, under the name of *Pearly Compound*, and later *Pearly Constituent*, was first described by Sorby in two consecutive papers to the Iron and Steel Institute :

   (a) *On the Application of very High Powers to the Study of the Microscopical Structure of Steel.* By H. C. Sorby. "Journal Iron and Steel Institute," 1886, p. 140, and

   (b) *On the Microscopical Structure of Iron and Steel,* ibidem, 1887, p. 253.

45. *Eutectic or Benmutic.* By H. M. Howe. "Metallographist," 1903, p. 167.

   Eutectic or Benmutic. By F. Osmond, ibidem, p. 243.

   Eutectic or Aeolic. By H. M. Howe, ibidem, p. 245.

   In an addendum to the last contribution Professor Howe has coined the term "eutectoid" now in universal use. There were also other suggestions, as, for instance, Professor Rinne's "Eutropian" point in meteorites.

   Physikalish-Chemishe Bemerkungen ueber Technishes und Meteorishes Eisen. By F. Rinne. "N. Jrb. fur Mineralogie, etc.," B. I, H. 3, Stuttgart, 1905.

   See also Link. "Zeitshrift phys. Chemie," 19, pp. 193–200.

46. Perhaps Sorby had in his mind such a process, when he wrote : ". . . these large crystals break up on further cooling into much smaller . . . these smaller crystals finally split up into alternating very thin plates."

On the Application of very High Powers to the Study of the Microscopical Structure of Steel. By H. C. Sorby, " Journal Iron and Steel Institute," 1886, p. 140. For further on granulation of pearlite, see:

(*a*) N. T. Belaiew. *Thesis,* 1909, pp. 16, 35–40.

(*b*) C. Benedicks. *A New Form of Pearlite.* " The Iron and Steel Times," 1909, May 6.

(*c*) *Notes on Pearlite.* By Howe and Levy. " Journal of the Iron and Steel Institute," 1916, pp. 210–232. Discussion of that paper by Dr. Rosenhain, p. 237.

(*d*) *The Inner Structure of the Pearlite Grain.* By N. T. Belaiew. " Journal of the Iron and Steel Institute," 1922, Spring Meeting, No. I, pp. 201–27.

47. *The Inner Structure of the Pearlite Grain.* By N. T. Belaiew. " Journal of the Iron and Steel Institute," May 1922, No. I, pp. 201–27.

48. Sorby gives for the thickness " of the thinner plates " the value of 1/80,000 of an inch, which gives approximately 0.3μ (" Journal of the Iron and Steel Institute," 1886, p. 143). The author's measurements are very close, ranging from about 0.4μ in the Alloy No. 1 to about 0.1μ in No. 8 (" Journal of Iron and Steel Institute," May 1922).

Lecture IV

STRUCTURAL EQUILIBRIUM IN SOLIDS

CONTENTS

LECTURE IV

STRUCTURAL EQUILIBRIUM IN SOLIDS

I. INTRODUCTION

THE regular geometrical form of a normally developed " idiomorphic " crystal is the result of an unhampered action of the directive *crystallisation force.*

Such crystals of the form of geometrical solids under favourable conditions are obtained in salts, as well as in minerals and metals. It is, however, very difficult to obtain such conditions, and consequently crystals reproducing, say, a regular cube or octahedron, are extremely rare.

It is more usual for crystals to appear with one or more faces abnormally developed or checked in growth; for instance, needle-like, or acicular, like crystals of free cementite, or, say, tabular plates of the same cementite in lamellar pearlite.

A still more usual appearance is that of *crystal skeletons* which occur when the linear velocities of crystallisation are great, and

consequently a regular and simultaneous growth of all the faces is rendered difficult by the intrinsic pressure of the liquid or the cohesion of the solid mass. So, as a consequence of the internal pressure, every growing crystal will be submitted to the action of *surface tension,* and will tend to assume the already mentioned dendritic or acicular forms.

Let us denote the amount of energy spent
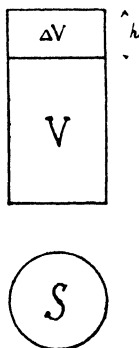
Fɪɢ. 35.—DIAGRAM TO ILLUSTRATE THE MECHANISM OF THE PROCESS OF CRYSTALLISATION.

from a certain nucleus during crystallisation by E. Let L be the linear velocity of crystallisation from that nucleus and σ the surface tension.

Let V be the volume of the crystal at a certain moment of its growth, and ΔV the increase of this volume per second. Let the area of the base of the volume ΔV be S, and its altitude h (Fig. 35) ;

then $\qquad \Delta V = S \times h$

and $\qquad E = \Delta V \times \sigma \qquad$ or

$\qquad E = S \times h \times \sigma.$

As $h = L$

$\qquad E = S \times \sigma \times L$

Let us suppose that L is very great. As σ is constant, the area S must become very small. The larger is L, the smaller will be the cross section of the crystal S, and the more will the crystal tend to assume the acicular or the thin needle-shaped form, suggesting, so to say, the shape having the least resistance to penetration. Such a form would seem to be the most suitable during the " *dynamic* " stage of the process.

Let us assume now that the crystal has finished growing, and that the crystallisation forces, having exhausted themselves in the rearrangement of molecules of a certain volume of matter, have ceased to work. Can the external form of such a crystal be considered now as stable ? The crystal in that new or " *static* " stage is submitted to the action of the same capillary forces as during the " dynamic " stage ; but· the action of these forces, or, as we usually say, of " surface tension," will tend most to lessen the total surface of the crystal and force it to assume the form with a minimum area (49). Such form will be, as demonstrated by Plateau, that of a sphere. If the crystals are small, such " spherodisation " will be accomplished

more easily and more completely ; if they are larger, only a certain curvature of the outlines would be attained. Moreover, in solids any considerable amount of spherodisation can be reached only at relatively high temperatures, when the mobility of the molecules of the matrix and of the crystal are sufficient to allow, what Dr. Stead called, " migration in solids."

II. Spherodisation in Eutectics and Eutectoids

A lamellar eutectic is built up of alternate layers of its constituents. These layers are usually extremely thin. For instance, the cementite lamellæ in pearlite are usually of the thickness of about $0 \cdot 1\mu$ ($100\mu\mu$). Consequently, their surface in proportion to the mass is very great, and the influence of surface tension at appropriate temperatures will be very marked.

Faraday's experiments on the effect of heat on very thin metallic leaves, subsequently confirmed and extended by Sir George Beilby (50), show the tendency of such leaves to retract and collect themselves into globular aggregates. The thickness of the films is given by Sir George Beilby as ranging from $10\mu\mu$ to $150\mu\mu$—that is to say, of the same order of magnitude as cementite lamellæ in a not too coarse pearlite. In Faraday's experiments the leaves of gold or

silver were supported on glass. In pearlite, alternate lamellæ support one another and the analogy is therefore very close.

The first experiments, clearly showing the change in shape of cementite lamellæ in pearlite on heating, were published by Dr. Stead in 1903 in a paper on *The Segregatory and Migratory Habit of Solids in Alloys and in Steel below the Critical Points* (51).

Examining an ingot of iron with 2% of phosphorus and a little carbon, Dr. Stead was able to show the change in the shape of cementite lamellæ during slow cooling through the 100° below the critical point. If the metal was cooled through that interval fairly rapidly, no change in the lamellæ was apparent. On the other hand, when the passage was very slow the extremities of lamellæ became knob-like, or even *bulbous*, suggesting the contraction of a thin film of water into a drop (Fig. 36).

The next stage would seem to be that of the formation of a number of drops, or of " spheres."

In 1909 Dr. Carl Benedicks published a paper on *A New Form of Pearlite*, where he described an intermediary stage of the process and gave photomicrographs of what he called " bead-like pearlite " (52).

This was obtained in grey pig-iron from Herrung, which had been heated to 670°; that

is, to just below the eutectoid transformation line. Small drawn-out globules were observed to form bead-like stretches, running parallel to the remaining laminated pearlite. After a longer annealing that form completely dis-

FIG. 36.—" PEARLITE FRINGE " (× 250).
(Stead, *Migratory Habit*, fig. 4.)

appeared and was replaced by coarse " granular " pearlite.

So the mechanism for the altering of the shape of the thin cementite lamellæ in pearlite under the influence of surface tension can be pictured as follows : First, the edges of the film become rounded, then the film itself begins to contract

into drawn-out grains, next these grains round themselves and coalesce into globular forms. The similarity between that process, the thin leaves of Faraday, and the breaking up of a thin layer of oil on water into globules, is very striking.

Pearlite, where the cementite has globularised, is called " globular " pearlite. The process is called by Howe " divorce," as lamellæ of cementite and ferrite are " divorcing " each other and assuming new structural forms. More generally the process is called " spherodisation."

This process, as shown by Goerens (53), can be accomplished even through heating only, if that heating is a very long one. This means that if the temperature is maintained for a sufficiently long time just under the eutectoid line, where the maximum mobility compatible with the existence of pearlite is allowed to the molecules, these, under the influence of surface tension, would tend to rearrange themselves in solids in the same sphere-like formations as in liquids.

In 1918, Whiteley, in a paper to the Iron and Steel Institute, showed that the process of spherodisation might be very much accelerated by previous cold work (54). A further interesting instance might be found in the Damascene process.

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III. SPHERODISATION IN THE PRESENCE OF THE EXCESS ELEMENT

The process of spherodisation proceeds much more easily and quickly in the presence of the excess or free element. So, for instance, pearlite divorces more readily in hypo or hyper than in eutectoid steels.

According to Dr. Stead, there is a certain attraction between cementite in pearlite and free cementite, and between ferrite in pearlite and free ferrite, the larger masses causing the smaller to coalesce and so tending to produce a complete structural separation (55).

These views were confirmed and expounded by Professor Howe in 1914 in a paper on *Structural Coalescence in Iron and Steel* (56).

The paper, together with the discussions in which Dr. Stead and Professor le Chatelier took part, must be considered as a standard contribution to the study of spherodisation.

In the author's alloys, referred to in previous lectures, the spherodisation range, that is, the area just below the eutectoid temperature, was passed extremely slowly, taking seven hours to cool down from 700° to 600°, and 17 hours from 700° to 500°. It was hoped, therefore, to find different stages of the process and to be able to closely examine the action of surface tension in solids (57).

PLATE XVII.
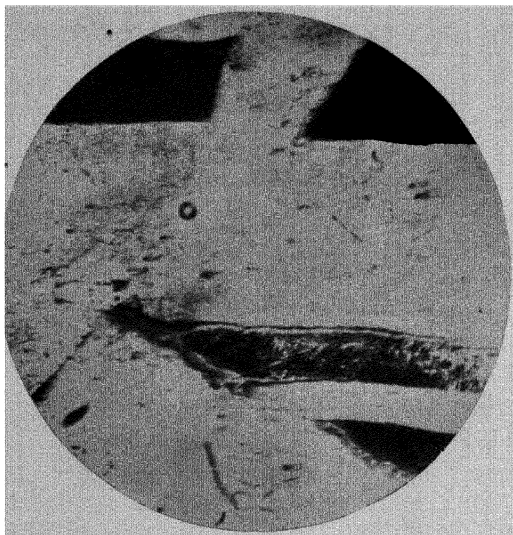
PHOT 26.—Alloy No. 8— × 400.
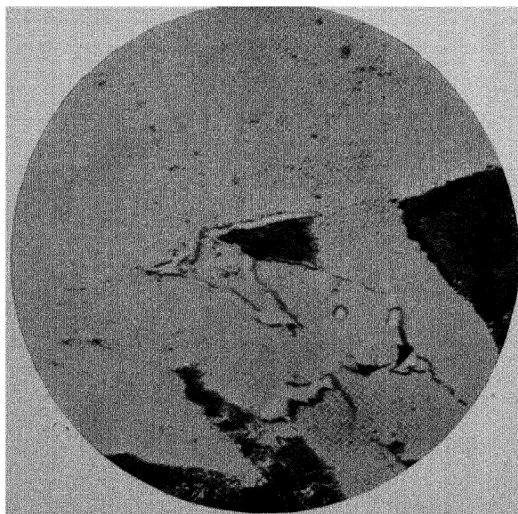
PHOT. 27 —Alloy No. 8 — × 400.
Various phases of spheroidisation of cementite in hypo-entectoid steel.

The most interesting alloy from that point of view proved to be the Alloy No. 8 (C = 0·55%) with the Widmanstätten structure. Islets of pearlite are embedded in the large masses of excess ferrite, forming the regular patterns of the Widmanstätten figures. The size of the islets varies very much, and it was expected that the working of the " crystallising attraction " on the smaller islets would be detected, as previously suggested by Stead. It was not possible, however, to find such developed " bulbous " pointings as in Stead's phosphoretic iron, but the next stage—where the bulbs were coalescing in one continuous mass around the pearlite islet—was traced in several places of the alloy.

Phot. 26 (Plate XVII) shows how every dark patch of pearlite is surrounded by an envelope of cementite, and even how these envelopes are connected with the cementite lamellæ of pearlite.

Let us suppose that the islet of cementite is small and drawn out. In such islets the cementite lamellæ are usually oriented perpendicular to the long axis. If in such islets the extremities of the lamellæ begin to " bulb " and coalesce, the whole mass might segregate into one plate and a complete " structural equilibrium " (58) be attained. Such a process in a far advanced stage of completion is shown by the small cementite needle of Fig. 37.

That needle has retained the orientation of the " primary " pearlite islet ; even small amounts of pearlite are still to be detected at both extremities.

Let us now suppose that the islet, being still very small, possesses an equiaxial form. If the

Fig. 37.—"STRUCTURAL EQUILIBRIUM," CEMENTITE AND FERRITE.
Alloy No. 8.—C = 0·55%
(× 100).

time afforded to the process be sufficient, all the ferrite lamellæ will be absorbed by the adjacent larger masses of the excess ferrite, and the contracting cementite lamellæ would gradually draw together and coalesce into a globule.

Phot. 27 (Plate XVII) shows the various

PLATE XVIII.—THE SPHERODISATION PROCESS STARTS.

PHOT. 28 - CRACKS ON A CEMENTITE NEEDLE.
Alloy No. 1— × 150.
(B. Brandt in the Author's Laboratory.)

stages of such a process: the larger mass of pearlite does not seem to be involved in it yet; a smaller islet is surrounded by an envelope of cementite, the smallest have already coalesced completely into so many globules.

Osmond detected such islets of pearlite surrounded by cementite in steels with a very small percentage of carbon and has given to them the picturesque name of " atolles "—reefy islands (59).

IV. SPHERODISATION OF CEMENTITE IN HYPER-EUTECTOID STEELS

Let us examine the structure of the Alloy No. 1 with 1·80% C. As every 1% of carbon means 15% of cementite, there is 27% of cementite in that alloy. These 27% of cementite are divided between the pearlite cementite (11%) and free cementite (16%). The 16% of cementite are distributed more or less evenly throughout the whole mass of the alloys, roughly suggesting the outlines of the primary dendrites (Plate II, Phot. 2).

The cementite agglomerations, if examined closely, will show that they are built up of small drawn-out prisms (Plate XVIII, Phot. 28). Sometimes these prisms emanate from one centre, sometimes they run roughly parallel one to another for a considerable length. There is a rough resemblance to the dendrites, and at a

first glance one would be inclined to call them by that name. But they are not dendrites at all—that is to say, these prisms or prismoids do not reveal the inner symmetry of their crystalline substance, as the axes of true dendrites do. A close examination will show that their orientation depends not on their internal symmetry, but on the external factor, as they run in accordance with the crystallographic structure of the gamma grain, just as in Widmanstätten structure. The author, therefore, in his thesis proposed for them the name of " pseudo-dendrites " (60).

Such a needle-shaped agglomeration of an extremely brittle substance cannot but make the whole mass brittle and unforgeable, and consequently useless. Fortunately, the force of surface tension may be called in for assistance, and transform the brittle needles into rounded drop-like forms. The cracked cementite needle of Phot. 28, Plate XVIII, shows perhaps the earliest stage of the process.

The following stages of the spherodisation process of a sample of hyper-eutectoid steel of 1·60% of carbon are shown on the next figures.

Phot. 29, Plate XIX, shows a thick vein of excess cementite, so to say, in the first stage of the process. The general outline remains seemingly the same as before, but all the sharp angles are thoroughly rounded up, changing the whole

PLATE XIX.
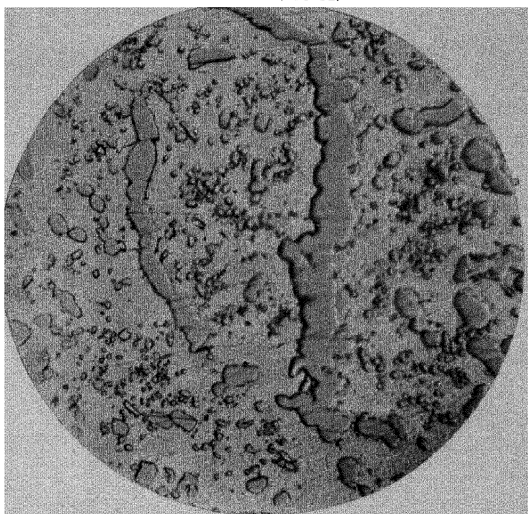
PHOT. 29.—f = 1·60" = × 1,000.
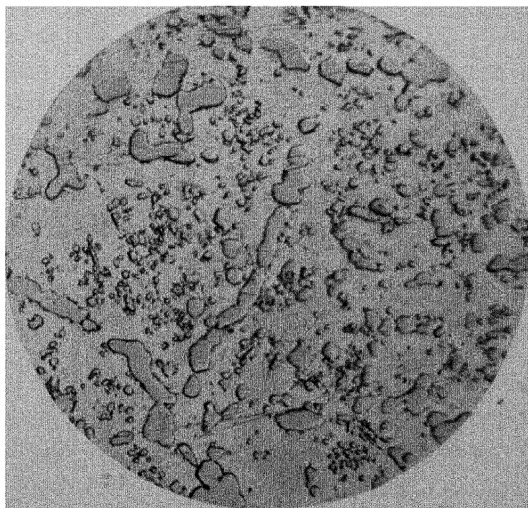
PHOT. 30.— C 1·60"   × 1,000.
(B. Brandt in the Author's Laboratory.)

PLATE XX.

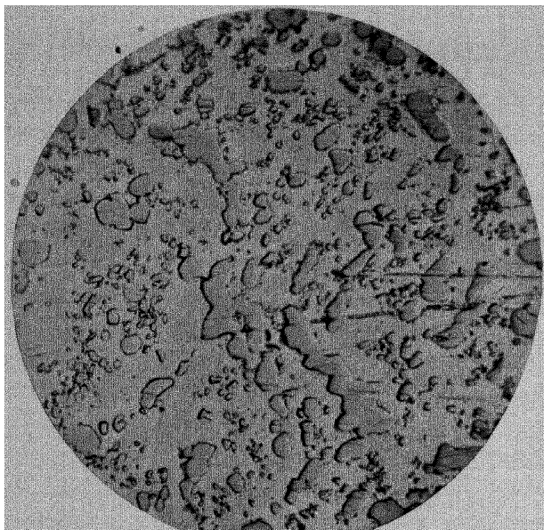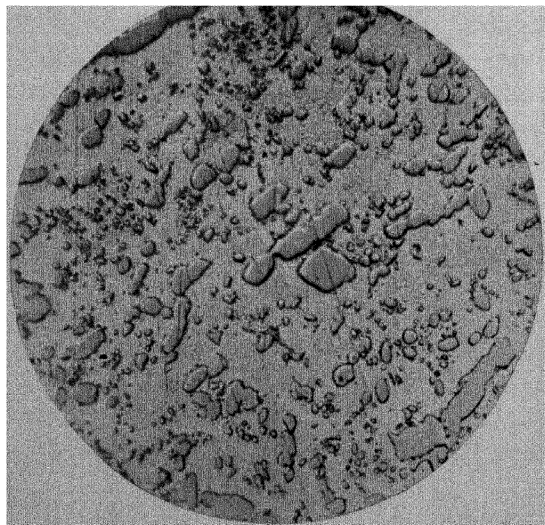PHOT. 31.—C = 1·60% — × 1,000.

PHOT. 32. Damascus Blade from the Author's collection.
C 1·60% — × 1,000.
(B. Brandt in the Author's Laboratory.)

appearance of the previous needle-shaped crystal into that of a flattened drop of viscous liquid. The smaller particles of pearlite cementite are completely spherodised already.

The next photograph, No. 30, may show the following stage, when the elongated particle of excess cementite begins to collect in five or six elongated globules, just like a thin elongated layer of water contracts into several drops.

A still further stage is reached on the Plate XX, where the whole of the excess cementite has collected into large globules.

As the solubility of very fine particles is greater than that of the larger ones, we could picture the last stage, when the small globules would be absorbed by ferrite and then gradually deposited on the larger ones, illustrating thus the " crystalline attraction " of Stead, and finally, collecting into one large globule or layer of cementite on ferrite.

Then the tendency towards *structural equilibrium* would be reached.

Such advanced stages of segregation are not to be met with in our solid alloys, but can be reproduced on liquids.

V. Some Theoretical and Practical Considerations

A very interesting case of the tendency towards structural equilibrium is presented by

the octahedric group of meteorites. The constituents of that group are camacite or nickel ferrite, the eutectoid plessite and taenite. These are arranged in Widmanstätten figures, and usually are of such large dimensions that the structure seems very coarse even to the naked eye.

F. Rinne (61) has pointed out that the analogy with the iron carbon alloys can be followed even in small details. So, for instance, in some of the meteorites taenite forms round the islets of plessite envelopes, which are strikingly like those of cementite round the pearlite islets, thus showing that the process of divorcing followed in both cases exactly the same laws.

The spherodisation of such brittle constituents, as cementite, is important from the practical point of view too. Such hyper-eutectoid steel, as already mentioned, could not be forged and shaped into suitable forms if the brittle lamellæ of cementite were not previously converted into globules. The ancient Damascene process seems to have unconsciously made full use of that property. In our modern processes, however, it seems that for one reason or another that process was rather underestimated, or even overlooked.

It might be interesting to mention that not only cementite, but carbides, for instance, in

alloy steels, can be easily spherodised, and the ductility of the steel increased (62).

Even impurities such as ferric oxide can be forced into globules and so made much less detrimental.

Many applications of the process might be also found in other alloys.

VI. The Damascene Process

One of the most, if not *the* most, fascinating instance of the process of spherodisation is the Damascene process.

The famous Indian steel, or wootz, was manufactured by that process from the earliest days, and found its way not only to Damascus, whence its name, but to all the neighbouring lands like Persia, Greece, and Rome. The Romans appreciated this steel very much, and so did Alexander the Great. During the Middle Ages this steel appeared in Russia, under its Persian name of " poulad," and in Western Europe, through Damascus, as Damascene steel (62).

The eighteenth-century travellers like Tavernier and Chardin were emphatic about it. Réaumur received some specimens from Cairo, but could find nobody in Paris to forge them.

Some specimens were brought to this country by Dr. Pearson and presented to the Royal Society (63). Faraday took a keen interest in

them and undertook extensive investigations, which resulted in his work in conjunction with Stodart on Alloy Steels (64).

In France, Bréant, the Examiner-General of Assays at the Royal Mint, presented to the Academy a brilliant paper on the composition of that steel (65).

For several years here and there a few papers were published on the subject, but gradually the interest began to die away.

Meanwhile, at Zlatoust in Russia, where the old caravan routes from Central Asia to Persia traversed the old Ural mining districts, Major-General P. Anossoff conceived the idea of finding out what was the reason of the watering, and of the qualities of the still mysterious Damascene steel. He conducted his investigations for several years, and finally, in 1837, was able to say that the problem was solved, and that the process was no longer mysterious to him. Beautiful swords manufactured by him bear testimony to his words (66).

In the course of his investigations, having noticed that the natives were able to gauge the quality of the article by its watering, or what we now call *macrostructure*, he began regularly to apply the microscope for investigating the microstructure, as shown in his journal (67).

Again the interest in that steel seemed to be

PLATE XXI.

Phot. 33.—DAMASCENE BLADE NO. 1 FROM D. K. TSCHERNOFF'S
COLLECTION.
× 5/4.
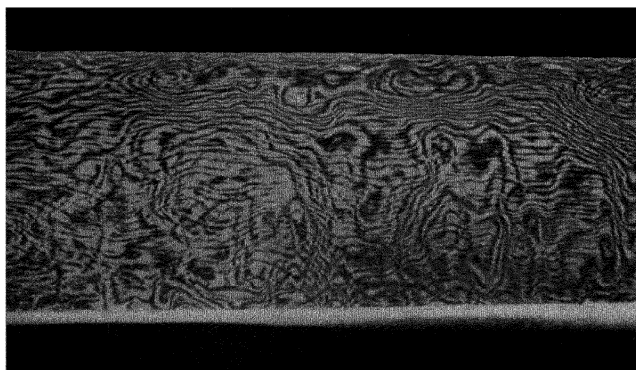
Phot. 34.—DAMASCENE BLADE NO. 1434 FROM THE WALLACE COLLECTION.

awakened.   Anossoff's swords were sent to the Hermitage at Petrograd ;   one of them was presented to Humbolt, Murchisson had another.

But gradually the interest died out, and the process itself fell entirely into oblivion.

In the sixties, D. Tschernoff, then a young metallurgical engineer, was sent on a mission to Zlatoust.   He met there one of Anossoff's old smiths, was deeply interested in what the old man had to say, and brought back to Petrograd some samples, and a deep interest in the Bulat (68).

Again many years passed.   Tschernoff was prevented by more important work from devoting himself to the mysteries of Damascene steel, but every year when lecturing at the Academy, in glowing terms he spoke of Anossoff and of Damascene steel, and urged his hearers to work out the Damascene process.

So fascinating were these lectures that many of his pupils became interested in " Bulat," and the lecturer among them.

The more he studied the question, the more interesting it seemed, one of the most interesting sides being perhaps the fact that the structure of old Indian blades proved to be that of perfectly spherodised cementite.

As the carbon content in these articles was very high—1·50, 1·60 and more—and the heating facilities were very poor, the alloys were

practically unforgeable. One can easily picture the old smith trying to forge a blade, and regretfully noticing that after one or two blows the cake had cooled down and had to be replaced in the furnace. Again some blows—light blows, as the hammer is a light one—this time the cake seems to be less obstinate, and shows some signs of ductility. Again it is heated, and again gently hammered. But each time its ductility increases, and finally it is as ductile as wrought iron.

The old smith has got his blade. It is perhaps rusted a bit ; he polishes it, rubs it with some old cloth wetted, maybe, in vegetable acids, and the beautiful structure is there.

To the next generation is passed the knowledge how to forge and how to etch. The buyer begins to appreciate the splendid watering, and to understand its relation to the mechanical qualities. So the first metallographic examination of the finished article became the custom of the Indians and Persians. Most of their knowledge was hidden from outsiders, and forgotten.

We had to rediscover it with our broader views and more perfect methods. Now we understand that the gentle forgings and subsequent heatings were exactly what was required to thoroughly spherodise all the cementite particles, and how by that procedure the *surface*

tension comes to our assistance and alters the structure so as to make an unforgeable alloy as ductile as copper.

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